ANNUAL PROGRAM REVIEW

HIGH-YIELD PULPING

March 25-26, 1998

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PROJECT F014

FUNDAMENTALS OF BRIGHTNESS STABILITY

DUES-FUNDED PROJECT SUMMARY
FY 1997-98

Project Title:	Fundamentals of Brightness Stability
Project Number:	F014
PAC:	Chemical Pulping and Bleaching
Division:	Chemical and Biological Sciences
Project Staff	
Faculty/Senior Staff:	Arthur J. Ragauskas
Staff:	Lenong Allison
FY 97-98 Budget:	Private Consortium - 72,000
Time Allocation	
Faculty/Senior Staff:	15% Ragauskas
Support:	50% Allison
Supporting Research	Fundamentals of Lignocellulosic Photostabilization Chemistry $102,000/2 years
	Gunnar Nicholson Exchange Program $40,000 - 1 year

RESEARCH LINE/ROADMAP:

<u>IMPROVED FOREST PRODUCTIVITY</u>:

- Develop modified/new pulping/bleaching processes
  - Chemical
  - High yield mechanical strength - high stable brightness
- Use of post treatments to give kraft properties
  - Chemical treatments
  - Mechanical treatments
- Modification of structure or composition of products

PROJECT OBJECTIVE:

Project activities are directed at investigating the fundamental chemical reactions that are initiated when high-yield pulps are photolyzed. As our knowledge of the photoxidation of mechanical pulp increases, methods to eliminate or significantly retard the yellowing process will be pursued.

GOALS FOR 97-98:

1) Examine role of starch, TiO_2, and $CaCO_3$ in brightness stabilization technology.

2) Prepare BCTMP/kraft test sheets with FWA, polymer additives, and antioxidants under simulated size press conditions and examine photoreversion properties.

3) Selective acylation of BCTMP to retard brightness reversion.

4) Prepare a brief review of the use of cross-linking textile additives and potential applications for mechanical pulp.

SUMMARY:

Research activities over the past year have been directed at four sub-projects:

1. Examine role of starch, TiO_2, and $CaCO_3$ in brightness stabilization technology.
Reversion studies examined the photostability of kraft - BCTMP handsheets treated with fluorescent whitening agents (FWA), TiO_2, $CaCO_3$, and starch. The results of these studies detected a decreased performance of FWA to retard photoyellowing. Interestingly, both $CaCO_3$ and TiO_2 were found to retard the rates of photoyellowing.

2) Prepare BCTMP/kraft test sheets with FWA, polymer additives, and antioxidants under simulated size press conditions and examine photoreversion properties.
Reversion studies of these treated handsheets were shown to retard reversion but nonetheless we could not achieve a photostable sheet in this type of approach.

3) Selective acylation of BCTMP to retard brightness reversion.
The acetylation and photoaging of BCTMP was studied. Accelerated reversion studies demonstrated that the photoreversion properties of acetylated BCTMP was dependent on the light source. Use of office lighting with acetylated BCTMP handsheets resulted in significant photobleaching of the treated sheets. These results suggest new research opportunities that could be exploited to halt brightness reversion.

4) Prepare a brief review of the use of crosslinking textile additives and potential applications for mechanical pulp.

The use of polycarboxylic acids to crosslink BCTMP fibers was explored. Although it was anticipated that this technology could improve strength and reversion properties of mechanical pulp, experimental results failed to detect improvements in the photostability of crosslinked BCTMP fibers.

FUNDAMENTALS OF BRIGHTNESS STABILITY

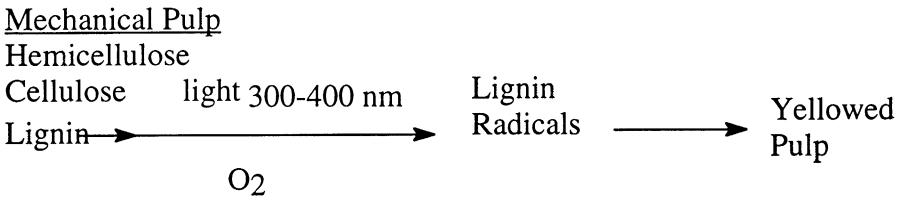
Brightness Reversion - Background

The photoyellowing of mechanical pulp has been a research issue of high priority for more than 30 years. During this time, our understanding of this phenomenon has significantly increased. Early investigations by Leary[1] and others[2] demonstrated that the absorption of near UV light (λ= 300-400nm) by the lignin component of mechanical pulp, in the presence of oxygen, leads to the yellowing. A variety of factors, such as pH,[3] metal salts,[4] bleaching,[5] moisture content,[3] and resin content[6] have been examined to determine their role in the brightness reversion phenomenon. To date, these investigations have not been successful in finding manufacturing conditions that significantly reduce the rate of photoyellowing for mechanical pulps.

The commonly accepted mechanisms for brightness reversion involves the absorption of a photon of light by extended conjugated structures present in lignin, such as α-carbonyl groups or olefinic structures conjugated with a phenyl ring.

It has been proposed that the excited state of these compounds leads to the formation of radicals; either directly, by an intramolecular bond cleavage process, or intermolecularly, via abstraction of a phenolic hydrogen. Alternatively, it has been suggested that the excited state could lead to the generation of singlet oxygen. This reactive species could then react further with lignin, generating a variety of radical intermediates. These lignin-based radicals then react further yielding colored material. Figure 1 summarizes these molecular effects.

Figure 1. Simplified schematic of brightness reversion process.



The chemistry associated with this process was reviewed in a Wood Grain Report issued to member companies in the fall of 1996.

Summary of Past F014 Results

The research objective of this project is to investigate the fundamental chemical reactions that are initiated when high-yield pulps are photolyzed. As our knowledge of the photoxidation of mechanical pulp has increased, we have placed a greater research

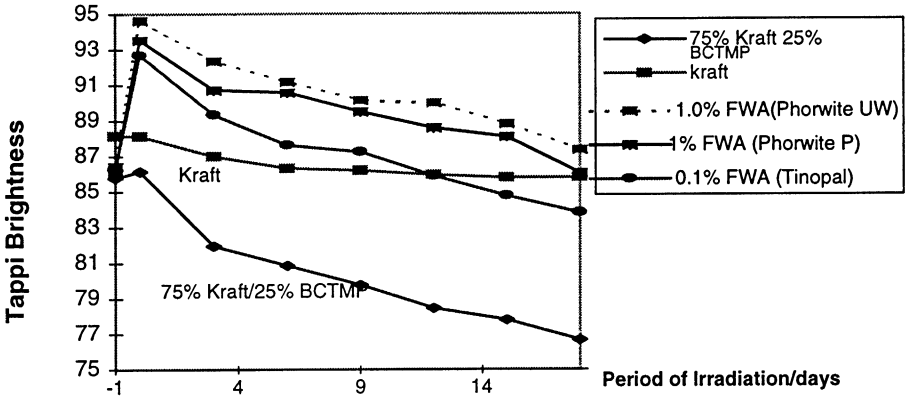
emphasis on examining new technologies that can retard and/or halt brightness reversion. Research efforts in this program have studied the photostabilization effects of radical scavenging agents such as ascorbic acid, thiosulfinates, and mercapto compounds. The photostabilization effects of UV-absorbers such as benzophenone and benzotriazole were also examined and shown to reduce the overall rates of brightness reversion. Nonetheless, the amounts of chemical required to retard reversion were considered too high for practical application. The use of a UV-absorber and a radical scavenger was shown to have synergistic effects that reduced the total amounts of additives needed while improving the overall photostability of the sheet.

Recently, our research studies have been directed toward evaluating the use of fluorescent whitening agents (FWA) to retard brightness reversion of mechanical pulps. The benefits of using a FWA as a UV-screen for mechanical pulp are two-fold benefit. First, the additive will enhance the initial brightness of a treated sheet and act as a UV-screen for harmful near-UV light. Second, it is known that mechanical pulps undergo photobleaching upon exposure to 400-450nm light and the addition of a FWA could potentially retard photoyellowing by contributing to this photobleaching effect.

Muller et al.[7] have reported that the use of FWA on CTMP paper provides a cost-effective means of economically achieving high apparent brightness values. Interestingly, the authors argued that financial benefits could be incurred by brightening CTMP sheets with FWA. Based on performance cost issues it was suggested that 3% FWA could be employed on mechanical pulps. FWA have been reported to be used in Canada for special advertising newsprint inserts employing 0.7 to 1.0% charge of FWA. In contrast to these reports, Doshi[8] has claimed that FWA will not brighten groundwood pulps as lignin can act as a quencher of optical brightening additives. This result suggests that FWA technology may be better suited for CTMP and BCTMP grades of pulp. A recent patent application has been submitted for the use of FWA agents on lignin-containing pulps that were treated with a reducing agent, such as sodium borohydride.[9] Bourgoing and Robert have also reported the effectiveness of FWA at retarding brightness reversion of several grades of mechanical pulp.[10] These reports demonstrate the continued interest in this field of photostabilization technology.

Over the past two years, we have examined several aspects of FWA treated BCTMP. The dose response of Tinopal, a commonly employed FWA, was explored with a series of BCTMP and BCTMP/kraft testsheets. Studies were directed toward evaluating the photostabilization effects of a FWA on 100% BCTMP. Figure 2 summarizes some of these results.

Figure 2. Photoreversion properties of BCTMP, kraft, and FWA treated BCTMP handsheets.

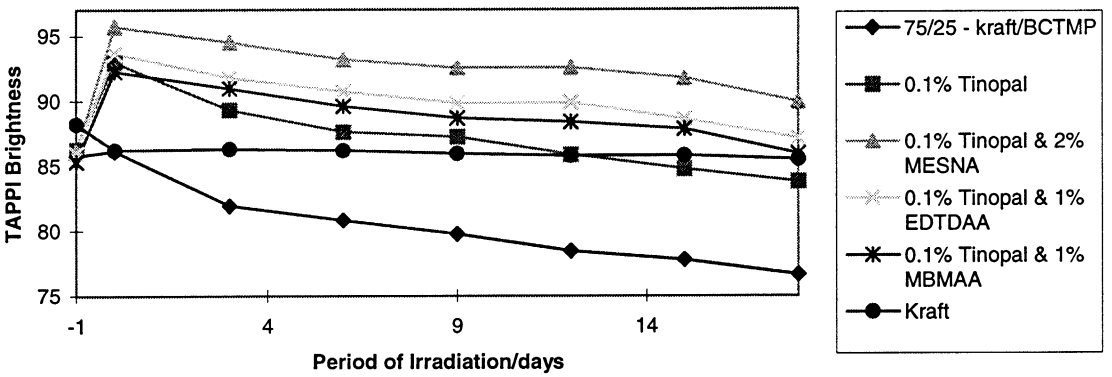


Note: Phorwite UW and Phorwite P are commercial FWAs

For handsheets prepared from 100% hardwood BCTMP, we determined that a FWA application level of 1-1.5% was optimal. Higher application levels of the FWA yielded lower initial brightness values and reduced photostabilization effects. This was attributed to the graying limit of the FWA. It is well known that when the fiber surface bonding properties for a fluorescent whitening agent are saturated the FWA will associate with itself. This effect prevents further "whitening" and a so-called graying limit is reached. Interestingly, testsheets prepared from 50% kraft and 50% BCTMP furnish appeared not to suffer from the same graying limit.

The use of a carrier molecule such as polyethylene glycol, polyvinyl alcohol, and carboxymethylcellulose has been shown to improve fluorescent whitening properties of FWA. For BCTMP pulps, we have shown that polyethylene glycol was an effective carrier molecule extending the fluorescent benefits of the FWA. Previous studies in this project have shown that radical scavenging agents such as MESNA [i.e., $HSCH_2CH_2SO_3Na$], ethylenedithio-diacetic acid [EDTDAA: $HO_2CCH_2SCH_2$-$CH_2SCH_2CO_2H$] or bismethylene(mercaptoacetic acid) [MBMAA: $HO_2CCH_2SCH_2$-SCH_2CO_2H] were particularly effective at retarding photoyellowing of BCTMP. The effects of these agents in the presence of Tinopal were explored employing testsheets from 75% bleached softwood kraft and 25% hardwood BCTMP. The results of these studies are summarized in Figure 3.

Figure 3. Use of Tinopal and co-additives to photostabilize 75% softwood kraft - 25% hardwood BCTMP testsheets.



These data indicates that all three additives were effective at enhancing the photostabilization effect of Tinopal. Perhaps most notable were the photostabilization effects of MESNA, since this reagent was the most effective and, due to its structure, does not exhibit the characteristic sulfur odor associated with thiol additives.

In addition to these studies, we have examined several other FWA performance issues, including the thermal reversion properties of FWA treated handsheets, use of differing HW and SW BCTMP furnishes, and the use of several different FWA.

Research Goals

FY 1997-98 goals for F014 are listed below:

1) Examine the role of starch, TiO_2, and $CaCO_3$ in brightness stabilization technology.

2) Prepare BCTMP/kraft test sheets with FWA, polymer additives, and antioxidants under simulated size press conditions and examine photoreversion properties.

3) Selective acetylation of BCTMP to retard brightness reversion.

4) Prepare a brief review of the use of crosslinking textile additives and potential applications for mechanical pulp.

These research goals have been accomplished over this past fiscal year and the results of these investigations are summarized in this report.

Results

Goal 1: The initial goal of this year's task was to evaluate the application of FWA additives with $CaCO_3$ and TiO_2 included in the sheet formulation. TAPPI handsheets were prepared from a mixture of HW BCTMP (25%), kraft (75%), and a series of additive mixtures including:

1) a. $CaCO_3$, b. $CaCO_3$ + 0.5% Tinopal, c. $CaCO_3$ + 0.5% Tinopal + 1% starch:
   d. $CaCO_3$ + 0.5% Tinopal + 1% starch + 1% PEG
2) a. TiO_2, b. TiO_2 + 0.5% Tinopal, c. TiO_2 + 0.5% Tinopal + 1% PEG

Note: Tinopal is a common commercial FWA

Treated and untreated handsheets were then exposed to office lighting over a prolonged time period and TAPPI brightness values (with and without fluorescence) were determined along with L*a*b* values. The results of these studies are summarized in Figures 1.1 - 1.3.

Figure 1.1. Photoreversion properties of 75% kraft - 25% BCTMP testsheets prepared with $CaCO_3$, Tinopal, starch, and PEG.

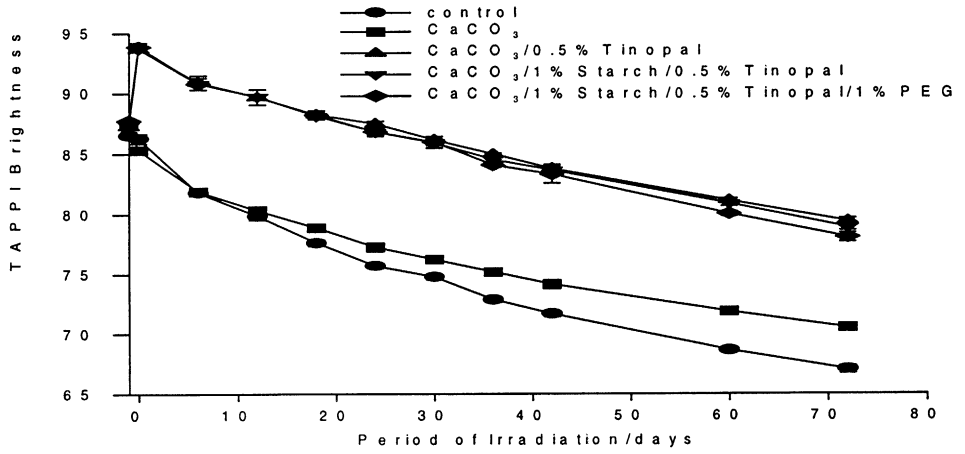
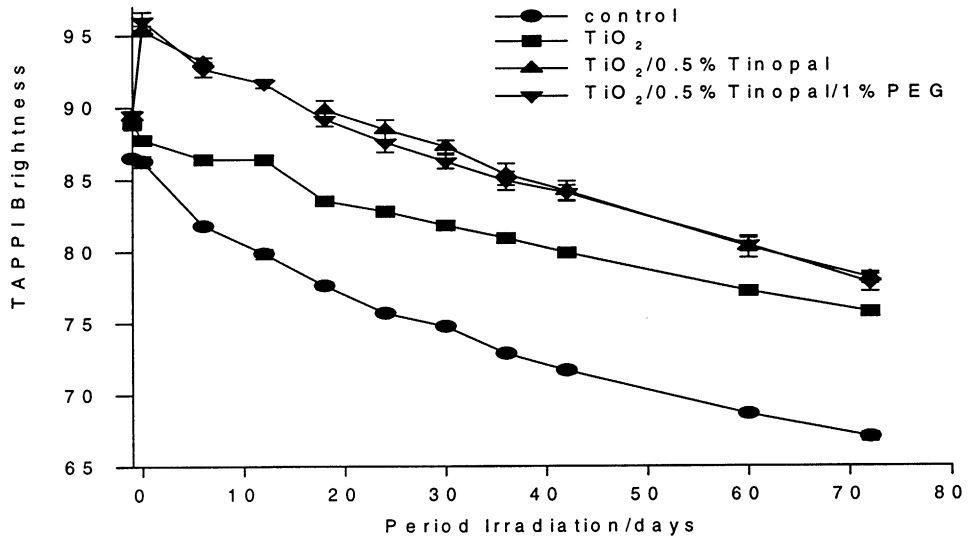


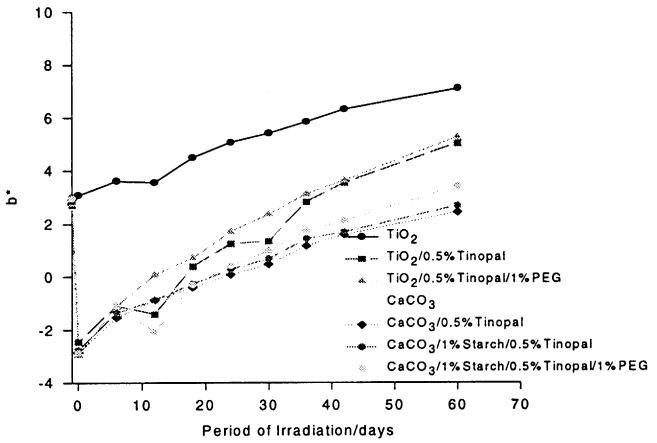
Figure 1.2. Photoreversion properties of 75% kraft - 25% BCTMP testsheets prepared with TiO_2, Tinopal, starch, and PEG.



The reversion data in Figures 1.1 and 1.2 illustrate several interesting trends. Calcium carbonate appears to retard the slow phase of photoreversion. TiO_2 exhibits a similar photostabilization benefit but these effects are larger and occur even in the early stages of brightness reversion. The use of TiO_2 on kraft-BCTMP testsheets appears to reduce reversion by 5 points in brightness after 72 days of continuous exposure to office lighting. Part of this photostabilization effect may be due to light scattering and absorption properties of TiO_2. These results are of particular interest since TiO_2 has been used in the cosmetic and paint industry to act as a UV-sunscreen. Its application for photostabilizing mechanical pulps has not been previously proposed.

The benefits of a FWA added to the furnish appears to increase only the initial brightness values. Additional studies using starch and Tinopal or starch + Tinopal + PEG yielded the same results. We remain uncertain if this is due to the application mode or if this is due to the interactions with the starch. The effects of these additives on L*a*b* values were determined. The b* values are presented below. Of special interest is the reduced rate of b* increase for the TiO_2 treated handsheets.

Figure 1.3. Changes in b* values for testsheets prepared from 75% kraft - 25% BCTMP, TiO_2, Tinopal, starch, and PEG.



In summary, both $CaCO_3$ and TiO_2 provide benefits for retarding photoreversion with the latter chemical providing especially effective photostabilization effects. The previously observed benefits of FWA with mechanical pulp seems to be diminished in the presence of the co-additives and/or method of preparing the sheet. The FWA, treated sheets still have higher initial brightness values but there appears to be little, if any, significant reduction in the overall rates of brightness reversion.

Goal 2: The second goal for this year was to apply a FWA (Phorwite UW:UW) and other photostabilization agents onto a sheet under simulated size conditions and study the reversion properties. The co-additives that were examined included:

1. PEG and polytetrahydrofuran-these polymers are both known to retard brightness reversion.
2. Ethylenebisthiopropionate, an antioxidant that has been shown to retard brightness reversion.
3. MgSO4, MnSO4, and NaCl were studied to determine if simple ionic materials could interfere with the observed reversion properties of the FWA-treated testsheets.

Employing a series of TAPPI handsheets prepared from 75% HW kraft and 25% HW BCTMP, the above additives were applied. The results of the reversion studies are summarized in Figures 2.1 to 2.4.

Figure 2.1. Photoreversion properties of 75% kraft - 25% BCTMP handsheets treated with (1% UW-10% PEG), (1% UW-1% PEG-0.5%EDTA), (1%UW-1%PEG-3.4%-polytetrahydrofuran) and an untreated sheet irradiated with office lighting.

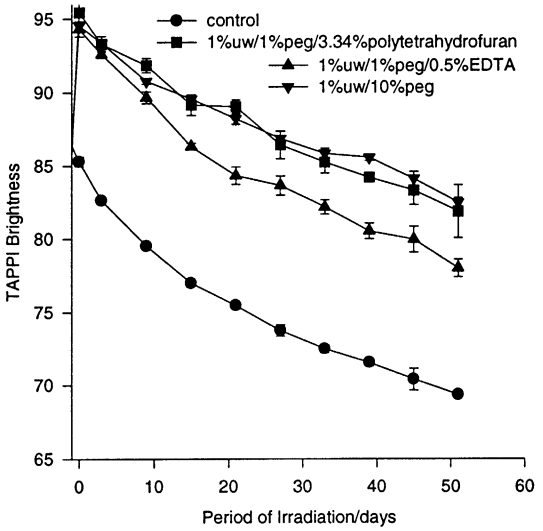
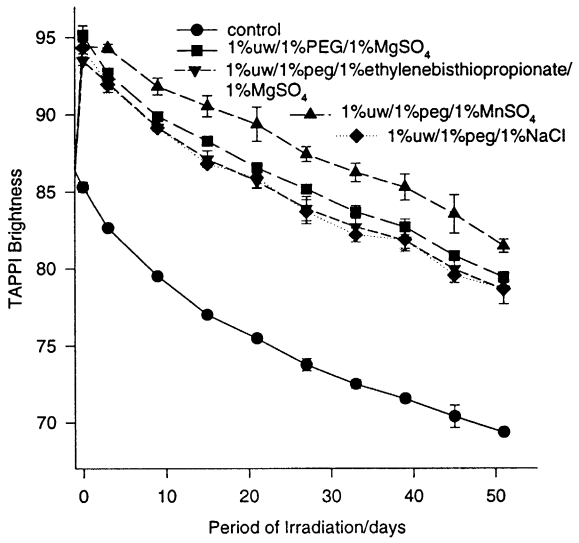


Figure 2.2. Photoreversion properties of 75% kraft - 25% BCTMP handsheets treated with (1% UW-1%PEG-1% $MgSO_4$), (1% UW-1%PEG-1%$MnSO_4$), (1%UW-1%PEG-1%NaCl), (1%UW-1%PEG-1% ethylenebiothiopropionate-$MgSO_4$) and an untreated sheet irradiated with office lighting.



The results of these photoreversion tests suggest that the use of UW and a polymer such as PEG or polytetrahydrofuran is effective at retarding brightness reversion. Currently, it is not possible to explain why UW/PEG/$MnSO_4$ appears to outperform other UW salt formulations.

An alternative means of analyzing the reversion data in Figures 2.1 and 2.2 is to measure TAPPI brightness values excluding the fluorescent. The results of this testing procedure are summarized in Figures 2.3 and 2.4 (see next page). This data exemplify the reduced rates of brightness reversion of the FWA-treated kraft/BCTMP handsheets and supports our previous conclusions on the use of FWA to retard photoyellowing.

Figure 2.3. TAPPI brightness values (excluding fluorescent) of 75% kraft - 25% BCTMP handsheets treated with (1% UW-10% PEG), (1%UW-1% PEG-0.5%EDTA), (1%UW-1%PEG-3.3%polytetrahydrofuran) and an untreated sheet irradiated with office light.

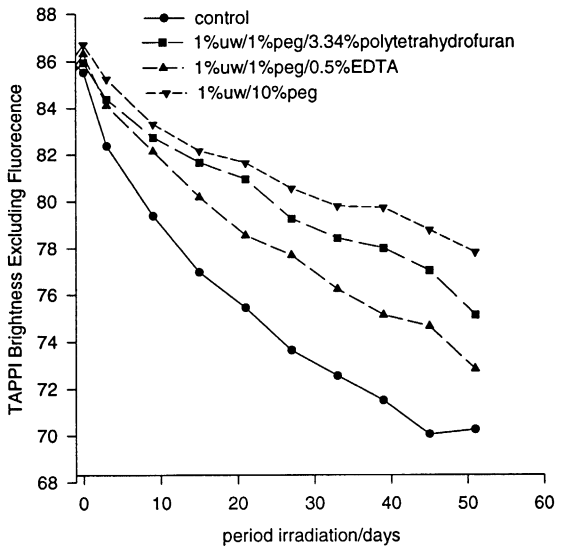
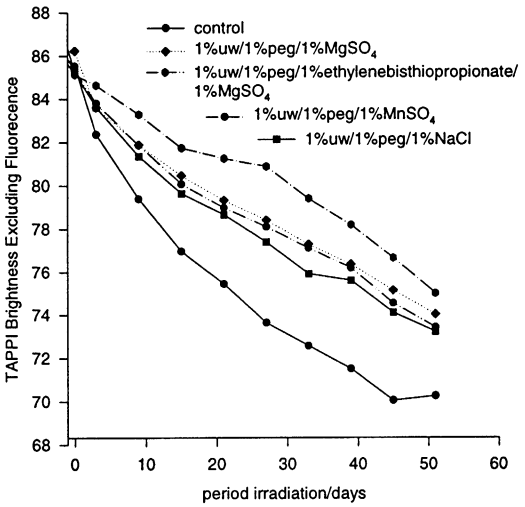
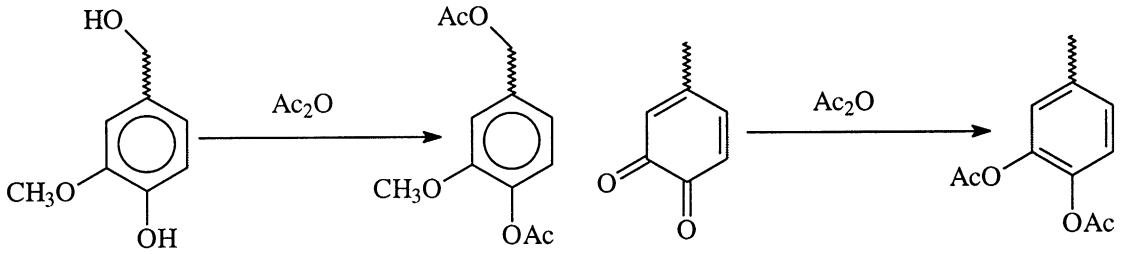


Figure 2.4. Tappi brightness values (excluding fluorescence) of 75% kraft - 25% BCTMP handsheets treated with (1%UW-1%PEG-1%$MgSO_4$), (1%UW-1%PEG-1%$MnSO_4$), (1%UW-1%PEG-1%NaCl), (1%UW-1%PEG-1% ethylenebiothiopropionate-1%$MgSO_4$) and an untreated sheet irradiated with office lighting.



The use of FWA can maintain +80 brightness sheets, for approximately 20 days of continuous irradiation with office lighting. The drawback with this approach is that we have not halted the yellowing process substantially. To address this issue, several other different technologies will need to be developed. The research described in Goals 3 and 4 begin to address this issue.

Goal 3. Measuring the effect of acetylating BCTMP to retard brightness reversion was one of the research goals proposed last fall. The acetylation of mechanical pulp has been known to retard the reversion of low brightness pulps. The proposed mechanism involves, in part, the acetylation of free phenoxy groups thereby blocking one of the key sites involved in the photoxidation of lignin to colored material, as shown below.



It is also suggested that acetic anhydride can react with *ortho*-quinones thus removing one of the most harmful chromophores present in mechanical pulp. It is interesting to mention that the acetylation procedure provides a mechanical pulp that photoyellows at rates less than those observed for methylated pulps. This result suggests that the photostabilization effects observed for acetylated pulp can not be due solely to the blocking of free phenoxy groups and supports the proposed reactions with *ortho*-quinones.

The acetylation reaction is accomplished by treating a mechanical pulp sheet with hot acetic anhydride (80-100°C) for varying periods of time (typically 5-15 min) and then washing away the excess material with water. Using this procedure on TMP or CTMP usually causes a loss in brightness of a few points. However, the resulting handsheets photoyellow at significantly slower rates than an untreated sheet. Prior to our research activities, most studies in this field had focused on TMP or CTMP grades of mechanical pulp.

The research activities in this field have involved a combination of F014 activities and studies funded by the Gunnar Nicholson Exchange Program. The latter studies were targeted at several issues including:

1. Studying the synergistic photostabilization interactions between known brightness stabilization additives and acetylated BCTMP. The results of these studies indicated that the use of a UV-absorber such as 2-hydroxy-4-methoxybenzophenone or Tinuvin 384 (a benzotriazole derivative) applied onto acetylated handsheets reduced the rate of photoyellowing by more than 90%. In contrast, the application of a FWA onto an acetylated pulp was found to be relatively ineffective. Application of polyethylene glycol or polytetrahydrofuran was also shown to be effective at reducing the overall rates of brightness reversion for both untreated and acetylated BCTMP handsheets.

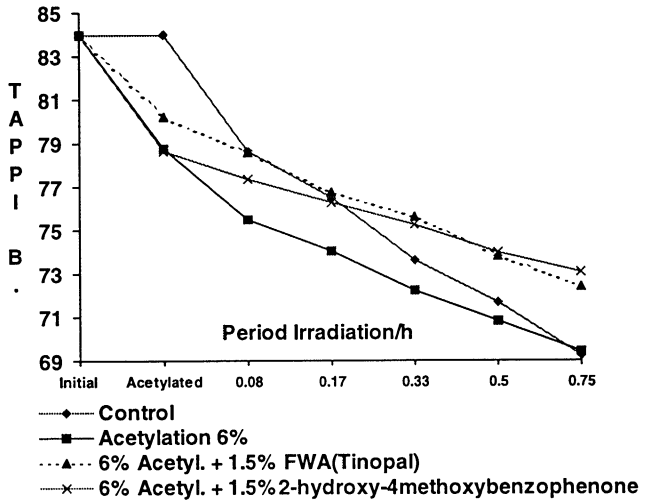
The results of this study are summarized in a manuscript titled "Chemical modification of lignin-rich paper Part 7. Photostabilizing high-brightness aspen CTMP by combining

various classes of additives and acetylation." A copy of this manuscript is attached to this report.

2. The effects of different light sources on accelerated photoreversion of untreated and acetylated BCTMP and TMP testsheets was studied. This investigation examined the effects of three different irradiation sources (e.g., ultraviolet "blacklight" fluorescent tubes, UV/VIS-fluorescent tubes, and a xenon lamp) on the photoyellowing properties of dithionite-bleached and hydrogen-peroxide-bleached spruce thermomechanical pulp, (TMP) and hydrogen-peroxide-bleached spruce and aspen chemithermomechanical pulp (CTMP). The photoaging response of additive-treated (e.g., UV-screen) and/or acetylated high-yield pulps toward the spectral distribution of the light source was studied. The order of light-induced discoloration, of the different high-yield pulps examined, was determined to be: hydrogen-peroxide-bleached spruce TMP>hydrogen-peroxide-bleached spruce CTMP>dithionite-bleached spruce TMP>>hydrogen-peroxide-bleached aspen CTMP (pretreated with hydrogen peroxide). The spectral distribution of the tested light sources marginally altered the aging response of the unmodified, dithionite-bleached, and hydrogen-peroxide-bleached spruce pulps. However, the high-brightness aspen CTMP showed some variation in the degree of brightness reversion.

This study discovered a previously unknown effect on the rates of brightness reversion of acetylated BCTMP. Figure 4.1 summarizes the overall rates of brightness reversion for a series of acetylated and untreated BCTMP handsheets exposed to a 300-400nm light source. The initial acetylation procedure caused a large drop in brightness (ca. 6 points) that would be very detrimental to any practical application. Upon exposure to 300-400 nm light, the acetylated sheets continued to suffer brightness reversion.

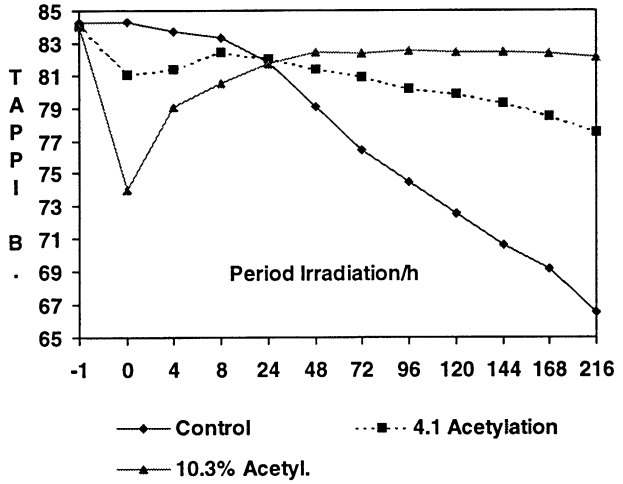
Figure 4.1. Photoyellowing properties of hardwood acetylated and untreated BCTMP using a 300 - 400nm light source.



Of greater interest is the photoreversion properties of the same handsheets exposed to office lighting under accelerated conditions. These results are summarized in Figure 4.2.

Clearly, the light source has a dramatic impact on reversion properties. The office light source appears to lead to photobleaching of the acetylated BCTMP. The impact of this photobleaching effect is so significant that within 8-24 hr of irradiation, the initial loss in brightness due to the acetylation treatment is practically recovered and the handsheets appear to be virtually photostable maintaining +79 brightness for 168 hr of continuous irradiation. It should be noted that after the same period of irradiation the untreated handsheet has a TAPPI brightness of approximately 69. A review of the literature indicates that this level of photobleaching and photostability has not been previously achieved.

Figure 4.2. Photoyellowing properties of hardwood acetylated and untreated BCTMP using an office light source.



Note: Time -1 is brightness prior to acetylation, time 0 is the brightness after acetylation.

The results of this research are summarized in greater detail in the attached manuscript titled "Chemical modification of lignin-rich paper Part 8. Effect of light source on the accelerated light-induced yellowing of untreated and acetylated high-yield pulps."

3. The third research area examined was the use of diffuse UV/VIS-reflectance to monitor the chemistry of brightness reversion for acetylated and untreated BCTMP. (Note: these studies were performed with the financial assistance of the Gunnar Nicholson Exchange Program) This study demonstrated that the wavelength distribution of the irradiation source strongly influenced the photochemistry of both untreated and acetylated pulps. Absorption difference spectra of aspen BCTMP, irradiated with a UV light source having a Gaussian spectral distribution between 300 and 420 nm (λ_{max}=350 nm), exhibited an apparent absorption maxima at 370 nm with a shoulder at 415 nm. Irradiation of aspen BCTMP with UV/VIS-fluorescent lamps exhibited an absorption peak at 360 nm in the UV/VIS reflectance spectrum and substantially less absorption in the entire visible region (λ>400 nm). Two major absorption peaks, at 330-345 nm and at 425 nm, were observed in the UV/VIS absorption difference spectra of irradiated spruce BCTMP regardless of the irradiation source used. However, in addition to the

photodiscoloration, a photobleaching with λ_{max}~390 nm was observed when the spruce BCTMP was irradiated with the two types of UV/VIS-fluorescent lamps. Acetylation was found to slow down the UV-light induced reactions, but could also promote photobleaching reactions when subjected to an irradiation source emitting light in the visible range. Generally, no further discoloration was observed when the acetylated BCTMP (acetyl content, 8-10%) was irradiated with the UV/VIS-fluorescent lamps under the aging conditions used in this work.

Further details of these studies are provided in the manuscript titled "Chemical modification of lignin-rich paper Part 10. The light-induced yellowing of untreated and acetylated high-yield pulps studied by solid-state UV/VIS diffuse reflectance spectroscopy."

Highlights of these research accomplishments were presented at the Fall PAC review in San Francisco. Recommendations from this review included:

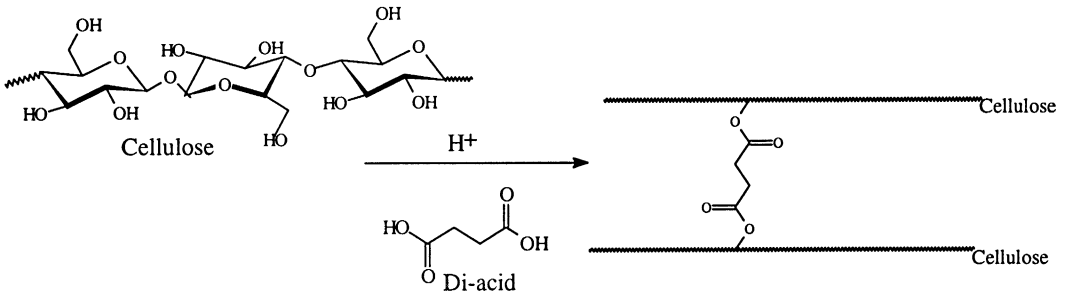
- The need to further understand the basic chemistry involved in the photobleaching effect of acetylated mechanical pulp.
- Explore the effect of acetic acid generated during the acetylation procedure on the overall photobleaching effect.

Based on these recommendations, we initiated new research sub-tasks. To address the issue that the acid generated during the acetylation procedure and/or during the photolysis was contributing to the observed photobleaching effect, we refluxed a sample of hardwood BCTMP in acid (0.015 N H_2SO_4). This pulp was then used to prepare handsheets so that their long term reversion properties could be studied. The acid treated sheets did not exhibit any improvements in the overall rates of brightness reversion. Likewise, the application of acetic acid onto a BCTMP only accelerated the reversion process. Both of these results suggest that the photobleaching effects observed for the acetylated BCTMP cannot be attributed simply to trace amounts of acid.

With the support of the PAC, it is proposed that the photobleaching chemistry of acetylated BCTMP be further investigated. The goal of this new sub-project would be to identify the underlying mechanism and exploit this knowledge to develop practical technologies for halting the photoyellowing process.

Goal 4. The final research goal for this past fiscal year was to examine the use of an alternative phenoxy blocking technology. The textile industry frequently employs cellulose crosslinking agents in the manufacturing of "permanent press garments." This chemistry makes use of polycarboxylic acids and a catalyst to crosslink fibers. Figure 4.1 summarizes the overall chemistry of permanent press.

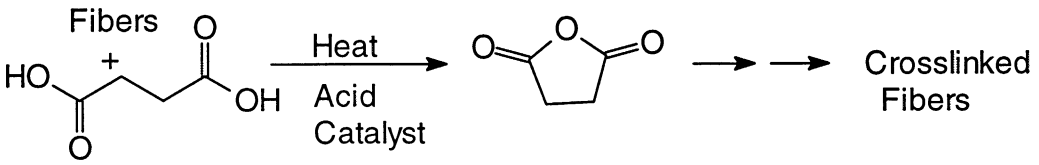
Figure 4.1. Chemistry of crosslinking cellulose fibers with polycarboxylic acid groups.



By extension, we had hypothesized that this technology could be utilized to crosslink mechanical pulp fibers via free phenoxy groups. (Note: fundamental chemistry suggests that cross linking phenoxy groups should be more effective than crosslinking cellulose hydroxy groups). In principle, this type of approach could retard reversion and improve sheet strength properties.

The proposed crosslinking chemistry requires a polycarboxylic acid and an inorganic phosphorus-containing acid. The mechanism for this reaction is believed to be initiated by heat. Upon heating a mixture of fibers, acid catalyst, and polycarboxylic acid a molecule of water is lost by the polycarboxylic acid and this generates a cyclic anhydride. (see Fig. 4.2) In the presence of the catalyst the anhydride then reacts with the hydroxy groups on the surface of the fiber.

Figure 4.2. Crosslinking mechanism.



In agreement with this hypothesis, only acids with at least three carboxyl groups per molecule are efficient crosslinkers (Note: the dicarboxylic acids can only produce single-ended attachments).

Most of the research in this field has been focused on tri- and tetracarboxylic acid cross-linking agents. The effectiveness of crosslinking textiles fibers is, 1,2,3,4-butanetetracarboxylic acid > aconitic acid (propenetricarboxylic acid) > tricarballylic acid (propanetricarboxylic acid) > citric acid (an *alpha*-hydroxytricarboxylic acid) > *cis*-1,2,3,4-cyclopentanetetracarboxylic acid. Because of severe discoloration when aconitic acid is used as a crosslinking agent, this polycarboxylic acid is not an attractive agent to use for crosslinking BCTMP fibers.

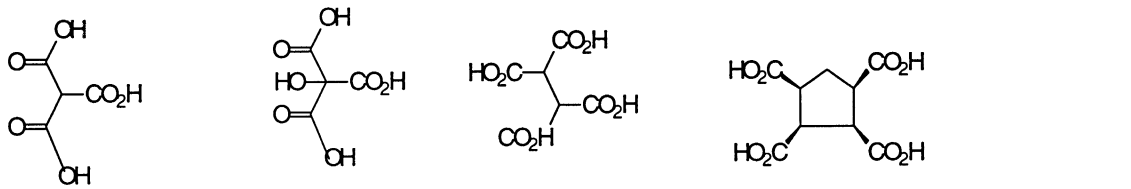
Suitable catalysts for this crosslinking process are alkali metal salts of hypophosphite, phosphates, and phosphites. The order of catalyst efficiency is

NaH_2PO_2>NaH_2PO_4>Na_2HPO_4. The mechanism of the catalysis is unknown, although the catalyst may be functioning as a buffering agent, keeping the pH levels within a desired range.

Although 1,2,3,4-butanetetracarboxylic acid is the most effective crosslinking agent, the compound is expensive. Citric acid is inexpensive, nontoxic (non-irritant to human skin, allowed to be used in food products), and readily available in commercial quantities. Citric acid is, therefore, the most interesting polycarboxylic acid studied in this sub-project. Figure 4.3 summarizes the polycarboxylic acids studied in this project.

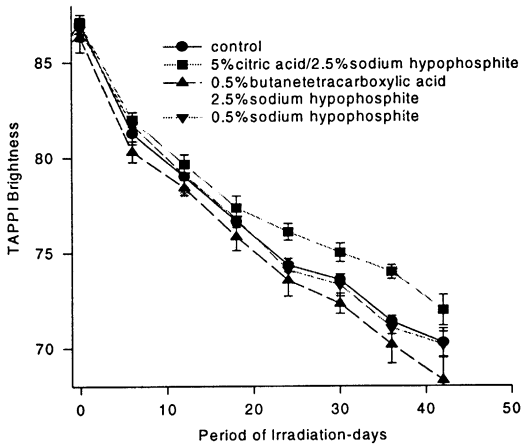
The crosslinking treatment procedure required immersing BCTMP testsheets in an aqueous solution of the polycarboxylic acid and catalyst for 30 sec. The saturated handsheets were then dried and characterized. (Note: initial testing employed handsheets containing 75% kraft/25% BCTMP and latter studies employed 100% BCTMP testsheets.)

Figure 4.3. Polycarboxylic acids selected for BCTMP crosslinking study.



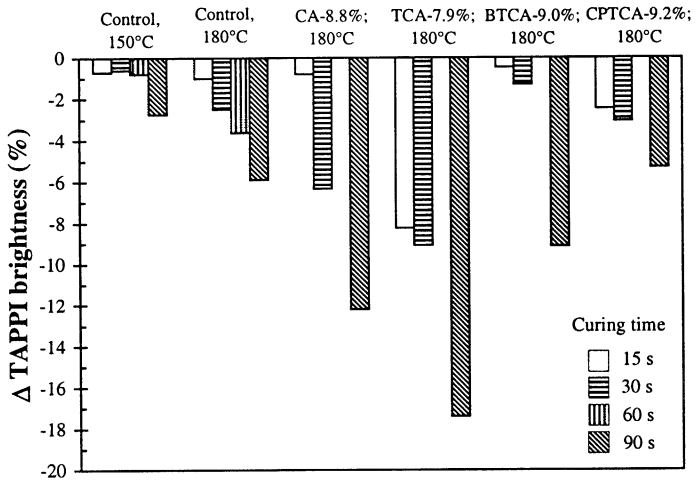
Preliminary studies examined the use of low-temperature (80°C, 5 min) curing for polycarboxylic acid treated BCTMP/kraft handsheets. The cured handsheets were then exposed to office lighting conditions and changes in TAPPI brightness were measured. Figure 4.4 illustrates typical reversion data we acquired for these additives.

Figure 4.4. Typical reversion properties for untreated and treated 75% kraft - 25% BCTMP handsheets when exposed to natural office lighting.



Since we were unable to achieve any benefits from the 80°C curing procedure, we then examined higher curing temperatures. For these studies, we employed TAPPI handsheets made from 100% HW BCTMP. After some initial investigations into curing temperature effects, we examined the use of 150°C and 180°C to cure the handsheets. Figure 4.5 summarizes the results of these studies. Unfortunately, the curing temperature detrimentally impacts the brightness of the sheet and the addition of polycarboxylic acids worsens this situation.

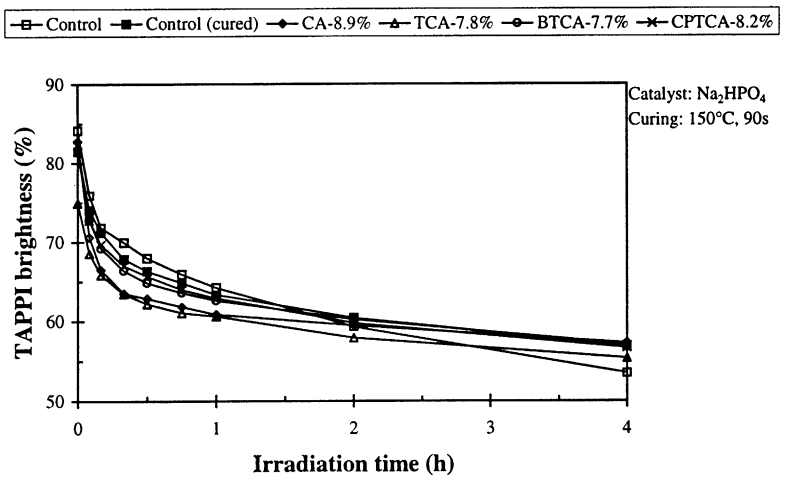
Figure 4.5. Changes in brightness upon curing untreated HW BCTMP handsheets and handsheets treated with CA, TCA, BTCA, and CPTCA.



Although the loss of several points of brightness from curing the polycarboxylic acid treated BCTMP handsheets would preclude commercial applications, we were interested in the resulting photoreversion properties of the cured handsheets. Figure 4.6 provides an

illustration of typical reversion data for the cured handsheets. These data indicate that the handsheets treated with polycarboxylic acids did not retard reversion.

Figure 4.6. Photoreversion of untreated and polycarboxylic acid treated HW BCTMP[1] handsheets irradiated with 300-400 nm light.



[1]control handsheet was not cured

Additional photoreversion data were acquired for all the testsheets described in Figure 4.5. However, these experiments failed to provide any indication that the polycarboxylic acid treated testsheets retarded photoreversion. On this basis, all further experimentation for this sub-project was halted.

Experimental

Materials: All pulps employed in these studies were acquired from commercial operations in Canada. All chemicals were commercially purchased and used as received. A 8000 MW PEG was employed for all studies.

BCTMP/Kraft handsheets were made following standard TAPPI methods. All optical measurements were performed in accordance with standard TAPPI test methods.

Preparation of alkaline handsheets: A 3:1 mixture of HW kraft and HW BCTMP were disintegrated in water (approx. 2% csc) for 15 min. A 15% charge of calcium carbonate and 0.2% charge of percol 175 as added to the pulp slurry and this mixture was stirred. The resulting pulp slurry was then used to prepare handsheets. In general, each handsheet contained approximately 1.2 g o.d. pulp and about 7-8 % $CaCO_3$ (Note: ca. 6% $CaCO_3$ drained from the sheet).

The PEG (MW:8000) and starch (CATO 15, from National Starch & Chemical Company) were applied onto formed handsheets.

The TiO_2 handsheets were prepared in a similar manner except that TiO_2 (5% charge)

replaced calcium carbonate.

Future Recommendations

The previously unidentified strong photobleaching effect of acetylated BCTMP offers new opportunities to effectively halt brightness reversion. At this time, very little is known of the chemical processes involved in this photobleaching effect. Future studies need to identify the exact mechanisms contributing to this effect and then develop new practical technologies that could utilize this photostabilization mechanism. The most important research issues that need to be addressed are:

- Isolate and characterize BCTMP lignin before and after acetylation procedure.
    - Use ball milled lignin or acid hydrolyzed lignin for model system;
    - Study changes in lignin structure during photobleaching by NMR, FT-IR, MW, and UV-VIS analysis.
- Examine alternative acetylation technologies for lignin in mechanical pulp.
    - Chemical treatments
    - Enzymatic catalyzed alkylation/acylation treatments.

Research Benefits

The anticipated benefits of these studies include:

- Development of new photostabilization technologies for high-yield pulps;
- Increased usage of high-yield fibers;
- Cost-effective new furnish for papermaking.

Supporting Literature

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Attached Articles

Chemical modification of lignin-rich paper

Part 7. Photostabilizing high-brightness aspen CTMP by combining various classes of additives and acetylation

Magnus Paulsson[1] and *Arthur J. Ragauskas*, Institute of Paper Science and Technology, Atlanta, Georgia, USA

Keywords: Acetylation, CTMP, Yellowing, Inhibition, Fluorescent whitening agents, Radical scavengers, Ultraviolet absorbers, Polymers

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SUMMARY: Different classes of additives (fluorescent whitening agents, polyethers, ultraviolet absorbers, and a radical scavenger) have been examined as photostabilizing agents for high-brightness, hydrogen-peroxide-bleached aspen chemithermomechanical pulp alone or in combination with chemical modification of the pulp (e.g., acetylation). The high-brightness CTMP was manufactured employing hydrogen peroxide both as a chemical pretreatment and as a bleaching stage. Both the acetylation treatment and the impregnation procedure were carried out on paper sheets.

Efficient inhibition of photoyellowing was obtained when moderate amounts of UV-screens, such as 2-hydroxy-4-methoxybenzophenone or Tinuvin 384 (a benzotriazole derivative), were applied onto acetylated handsheets; more than 90% of the yellowing was hindered by this treatment. Impregnation with fluorescent whitening agents had little effect in reducing the overall discoloration, although some photostabilization effect was observed when they were applied onto unacetylated paper sheets at relatively high application levels. Prolonged irradiation and application onto acetylated paper sheets strongly reduced the effectiveness of the fluorescent whitening agents. Among the other tested additives, polytetrahydrofuran showed the best result in preserving the brightness during irradiation both alone and in combination with acetylation.

With regard to the overall effect of acetylation, i.e., the brightness loss during reaction and the slightly lower efficiency in retarding yellowing compared with other acetylated bleached high-yield pulps, the results (under the conditions examined) indicate that the pretreatment step with hydrogen-peroxide introduced leucochromophoric structures that were detrimental to the aging properties of the acetylated pulp.

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High-yield pulps such as groundwood pulp (GWP), thermomechanical pulp (TMP), and chemithermomechanical pulp (CTMP) use the world's wood resource in an efficient and environmentally friendly way. This is because mechanical pulps contain all three major components of wood (e.g., cellulose, hemicelluloses, and lignin) unlike most chemical pulps that largely utilize the cellulose wood component. Today, it is possible to produce high-yield pulps at less than half the cost of chemical pulps and with brightness and strength properties that permit their use as substitutes for chemical pulps in many high-quality printing and writing papers (Levlin 1990; Stanley, Priest 1994; Mackie, Styan 1995; Ford, Sharman 1996). The major remaining obstacle to the wider utilization of these pulps in high-value furnishes is their tendency to undergo thermal and especially light-induced discoloration. If the brightness stability could be improved, the market for bleached mechanical pulps, particularly high-brightness chemithermomechanical pulps, would increase significantly (Cockram 1989).

Brightness reversion of high-yield pulps may be caused by heat or light. Thermal oxidative discoloration, depending on both temperature and humidity, can be a problem during pulp production. Because paper is not normally exposed to high temperature in combination with high humidity, the brightness loss caused by heat is usually of minor importance (even after long storage times). The photochemical oxidative discoloration is the most damaging, and can result in a brightness decrease of more than 30 brightness units in a short period of time. Under identical conditions, the rate of yellowing of mechanical pulp is about 10 times that of fully bleached kraft pulp, and hence, high-yield pulps cannot be used in products where brightness stability is essential (Heitner 1993).

The light-induced yellowing mechanism includes several complex reactions that are today not completely understood, although much progress has been made in the last decade in understanding some of the key steps in the discoloration process (cf. Gratzl 1985; Heitner, Schmidt 1991; Leary 1994; Paulsson 1996). It is generally accepted that the main photochemical reactivity is associated with the high lignin content of mechanical pulps (Forman 1940; Nolan et al. 1945; Leary 1968; Kringstad 1969). However, it has been suggested that the yellowing, to some extent, may be attributed to pulp constituents other than lignin (e.g., cellulose and hemicelluloses) or to other factors such as the presence of metal ions and moisture (Giertz 1945; Rapson, Spinner 1979; Gellerstedt et al. 1983; Janson, Forsskåhl 1989; Németh et al. 1992). Insufficient knowledge of the reactions leading to discoloration has made it difficult to develop methods that are technically and economically feasible in preserving the brightness of the bleached high-yield pulps.

Several approaches have been undertaken to photostabilize lignin-containing pulps. The proposed treatments can be divided into two categories, i.e., addition of inhibitors and chemical modification. The first category is characterized by the addition of compounds such as ultraviolet absorbers (which reduce UV-light absorption by pulp), antioxidants (which trap intermediate radicals), and quenchers (which inactivate excited molecules). The treatments in the second category function by suppressing the formation of chromophores by chemical modification of functional groups in the lignin moiety.

Among the ultraviolet absorbers (UV-screens) tested, 5-phenylpenta-2,4-dienoic acid, 2-hydroxy-benzophenone, and benzotriazole derivatives have shown the best effect in retarding yellowing (Nolan 1945; Kringstad 1969; Gellerstedt et al. 1983; Fornier de Violet et al. 1990; Castellan et al. 1994; Davidson et al. 1995; Pan et al. 1996). Ascorbic acid has been reported to stabilize hydrogen-peroxide-bleached mechanical pulps, but the inhibition effect was only temporary; ascorbic acid is consumed, and the discoloration is merely delayed (Janson, Forsskåhl

1989; Fornier de Violet et al. 1990; Schmidt, Heitner 1991; Agnemo 1992; cf. Grimsley et al. 1989). Ascorbic acid inhibits yellowing by functioning as a radical scavenger and reduces the phenoxyl radicals formed (Wan et al. 1993). The inherent thermal instability of ascorbic acid is, however, a serious limitation for the use of this antioxidant (Ragauskas 1994). Complexing agents such as tartaric acid and gluconolactone can also partially protect high-yield pulps against ultraviolet radiation (Janson, Forsskåhl 1989). Hydrogen-donating compounds such as sodium formate (Francis et al. 1992) and 2,5-dihydroxydioxane (Francis, Evans 1994) have also been proposed as inhibitors of light-induced yellowing. Sulfur-containing compounds, the sodium salt of thiodipropionic acid, 1-thioglycerol, glycol dimercaptoacetate, thioglycolic acid, methylthioacetic acid, sodium formaldehyde sulfoxylate (Rongalite), polyethylene glycol dithiol, and 1-dodecanethiol have all shown some effect in preventing discoloration of lignin-containing pulps (Kringstad 1969; Cole, Sarkanen 1987; Janson, Forsskåhl 1989; Fornier de Violet et al. 1990; Daneault et al. 1991; Cook et al. 1996; Pan, Ragauskas 1997). Recent research has shown that 2,2'-oxydiethanethiol, ethylene glycol bis-thioglycolate, 3-mercapto-1,2-propanediol, and 2,2'-dithio-2-oxodiethanol were effective in preventing light-induced brightness reversion of bleached CTMP (Pan, Ragauskas 1995a, b; Ragauskas, Cook 1997). The stabilizing activity of thiols is, however, reduced on long-term storage. Furthermore, the unpleasant odor that most of the sulfurous compounds possess could be a serious problem restricting the field of application. Among the phosphorous compounds tested, sodium hypophosphite was efficient probably because of its reducing capacity (Fornier de Violet et al. 1990; Davidson et al. 1991). Recently, Guo and Gray (1996) showed that sodium hydroxymethylphosphinate, a stable, water-soluble, colorless, and odorless phosphorous compound, was efficient in retarding the light-induced yellowing of hydrogen-peroxide-bleached CTMP (cf. Guo et al. 1997). Polyethylene glycol (PEG) with different molecular weights and different end groups can be used to prevent yellowing if relatively large amounts are added (Minemura 1978; Janson, Forsskåhl 1989; Forsskåhl, Janson 1992; Cole et al. 1993; Maiocchi et al. 1994; Davidson et al. 1995; Janson et al. 1995). Polytetrahydrofurans (PTHF) were found to both brighten and photostabilize different mechanical pulps, whereas polypropylene glycol (PPG) showed only a weak effect, and polyvinyl alcohol (PVA) showed no effect in retarding the brightness reversion (Janson et al. 1995; Janson, Forsskåhl 1996). The protective mechanism of polyglycols (or other polyethers) is still not well-known, although complexing ability, antioxidative effects, and changes in migratability may be considered (Janson et al. 1995, Janson, Forsskåhl 1996). Recently, Ragauskas (1993) reported that 2,4-hexadienol and related unsaturated systems were effective additives to retard yellowing of bleached hardwood CTMP (cf. Pan et al. 1996). Hexadienol stabilizes mechanical pulps, in part, by triplet quenching of the excited state of lignin chromophores (Harvey, Ragauskas 1996).

The chemical modification approach of potential chromophoric or leucochromophoric groups in lignin involves reduction of α-carbonyl groups (Manchester et al. 1960; Andrews, Des Rosiers 1966; Leary 1968; Lin, Kringstad 1970; Tschirner, Dence 1988; Fornier de Violet et al. 1989; Ek et al. 1990; Francis et al. 1991; Schmidt, Heitner 1991; Castellan et al. 1992a; Paulsson et al. 1995), hydrogenation of ring-conjugated ethylenic groups (Lin, Kringstad 1970; Tschirner, Dence 1988; Castellan et al. 1992b; Hu et al. 1997a, b), and acylation or alkylation of hydroxyl groups (Manchester et al. 1960; Andrews, Des Rosiers 1966; Singh 1966; Leary 1968; Wallis, Wearne 1982; Tschirner, Dence 1988; Ek et al. 1992; Castellan et al. 1992a; Paulsson et al. 1995; Paulsson et al. 1996). Among these treatments, acetylation has shown the best effect in improving the long-term photostability of both unbleached and hydrogen-peroxide-bleached

pulps at a low extent of derivatization. This can be achieved with retained or even considerably improved strength properties (e.g., in the wet state) provided that the paper product instead of the pulp is acetylated (Paulsson et al. 1994).

The present paper describes the photostabilizing effect of acetylation alone or in combination with various classes of additives (UV-screens, polymers, and a radical scavenger) for high-brightness hardwood (aspen) CTMP. The possibility of using optical brightening agents (fluorescent whitening agents) as inhibitors for yellowing is also discussed.

Experimental

Pulps and paper samples. Commercially produced hydrogen-peroxide-bleached aspen (*Populus tremuloides*) CTMP was used as received for the studies described in this paper. The pulp was obtained as dried sample. The high-brightness CTMP was manufactured employing hydrogen peroxide both as a chemical pretreatment and as a bleaching stage. Handsheets (60 $g \cdot m^{-2}$) were prepared according to TAPPI Test Method T 205 om-88. The paper sheets were then conditioned at 23°C and 50% r.h. according to TAPPI Test Method T 402 om-88 before further treatment.

Solvents and photostabilizing additives. All solvents and additives; polyethylene glycol (average molecular weight 600 and 3400), polytetrahydrofuran (average molecular weight 250), 2-hydroxy-4-methoxybenzophenone, Tinuvin 384 (a benzotriazole derivative supplied by Ciba-Geigy Corporation), 2-mercaptoethanesulfonic acid monosodium salt and the fluorescent whitening agents Phorwite UW Liquid (Bayer Corporation), and Tinopal SFP (Ciba-Geigy Corporation) were commercial products and were used as received. Footnotes in Table 1 give the chemical composition of the fluorescent whitening agents and the UV-screen Tinuvin 384. Formulas for the examined additives are shown in appendix 1.

Acetylation procedure. The bleached CTMP handsheets [cut into strips (30 x 75 mm)] were acetylated (at 100°C or 110°C) according to the procedure described by Paulsson et al. (1994).

Impregnation procedure. Weighted amounts of additives were dissolved in water, methanol, or acetone and sprayed onto handsheets to obtain various levels of addition. At least duplicate tests were performed.

Analyses. The acetyl content was calculated from the amount of acetate liberated after saponification with sodium hydroxide as previously described in Paulsson et al. (1996). The acetyl content is given as a percentage of the dry paper. The phenolic hydroxyl content was determined according to the procedure described by Lai et al. (1990). The amount of photostabilizing additive applied onto the handsheets was determined by weighing the handsheets prior to addition and after reequilibrating of the treated handsheets (at 23°C and 50% r.h.). The addition level is given as a percentage of the conditioned weight of the paper.

Accelerated light-induced yellowing. The paper samples were subjected to an accelerated photoyellowing in a Rayonet photochemical reactor (Model RPR 100, The Southern New England Ultraviolet Company, Branford, CT, USA) equipped with eight RPR 3500Å UV-lamps ("blacklight," The Southern New England Ultraviolet Company) and a merry-go-round apparatus for uniform irradiation. The temperature was kept close to room temperature by a cooling fan (to minimize heating of the sample). Untreated paper sheets were used in all radiation experiments as controls.

Optical measurements. TAPPI brightness, fluorescence, and color changes [according to the CIELAB color scale (L^*-, a^*-, b^*-values)] were measured using a Technidyne Brightimeter

(Model S-5) according to TAPPI Test Method T 452 om-92 and TAPPI Test Method T 524 om-94. The post color (PC) number (at 457 nm, according to Giertz 1945) was calculated for the treatment with inhibitor and/or acetylation (PC_1) and for the light-induced reversion (PC_2) (cf. Janson, Forsskåhl 1989). The sum of PC_1 and PC_2 represents the total effect of the treatment: $PC = PC_1 + PC_2$.

Results and discussion

The effect of irradiation on the yellowing of additive-impregnated, high-brightness aspen CTMP

To assess the brightness reversion properties of additive-treated, high-brightness hardwood CTMP, a series of test sheets were impregnated with various classes of inhibitors, as summarized in Table 1. The additives studied were two polymers: polyethylene glycol (PEG, molecular weights 600 and 3400) and polytetrahydrofuran (PTHF, molecular weight 250); two optical brightening agents (fluorescent whitening agents, diaminostilbenedisulfonic acid derivatives): Phorwite UW Liquid and Tinopal SFP; two UV absorbers: Tinuvin 384 (a benzotriazol derivative) and 2-hydroxy-4-methoxybenzophenone (HMB); and a radical scavenger: 2-mercaptoethanesulfonic acid, monosodium salt (MESNA).

As can be seen in Table 1, the addition of PEG 600 did not change the brightness value to any great extent, whereas a slight brightening effect (negative PC_1) was observed for the PEG 3400- and/or PTHF 250-treated sheets. The effect of increasing application level was small as was the effect of combining the two polymers PEG 3400 and PTHF 250. These results differ from those of Forsskåhl and Janson (1992). They found that aspen pulps (GW and CMP, both unbleached and dithionite or hydrogen-peroxide-bleached) were discolored (about 3.5 brightness units) on impregnation with PEG 600, whereas the corresponding spruce pulps were brightened. The difference in mechanical pulp type (CMP versus CTMP) could possibly explain the difference in results obtained. The increase in brightness due to treatment with polytetrahydrofuran has been attributed to an increase in the light scattering ability of the treated paper (Janson, Forsskåhl 1996). Both the fluorescent whitening agents, Phorwite UW Liquid and Tinopal SFP, increased the TAPPI brightness values to above 90. The application level to reach 90+ brightness values was higher for Phorwite UW Liquid (2.8%) than for Tinopal SFP (1.1%). This is because Phorwite UW Liquid contain less of the active fluorescent substance, a diaminostilbenedisulfonic acid derivative (ca. 15% by weight) than Tinopal SFP (ca. 75% by weight). It is also evident that the graying limit for Tinopal SFP is reached when the charge level is about 1%. An increase in the amount applied above this level will therefore not increase the brightness further. The action of optical brightening agents is based on fluorescence; they have the ability to absorb ultraviolet radiation and re-emit visible blue light. The yellow cast of the paper is shifted toward blue, which can be seen as a decrease in the value of the CIELAB color coordinate b^* and an increase in the value of the coordinate a^* (Table 1). The addition of the UV absorber Tinuvin 384 resulted in a slight brightness loss of less than one brightness unit, whereas the benzophenone-treated handsheets lost up to four units depending on the charge level used. The brightness loss for the HMB-treated sheets is due to its UV-visible absorption (λ_{max} = 323 nm) that tails into the visible range. Impregnation with the radical scavenger MESNA increased the brightness value with up to two brightness units. This is probably an effect of its hydrogen-

donating ability to certain unsaturated colored structures in the lignin moiety, i.e., to coniferaldehyde and quinonoid units.

The effect of accelerated light-induced aging of untreated and impregnated hydrogen-peroxide-bleached CTMP sheets is summarized in Table 2 and Figs. 1-4. Generally, irradiation decreased brightness, increased b^*, and decreased L^* for all handsheets. This is equivalent to a more yellow color of the paper. The photostabilizing effect of the two polyglycols was moderate, at least at low charge levels. The different molecular sizes did not generally alter the performance of the polymer. The other tested polyether, polytetrahydrofuran, was somewhat more efficient in retarding yellowing. The degree of reversion, measured as post color number (PC_2), after 4 hours of irradiation was 10.2 for the PTHF-impregnated sheets with the highest charge level (6.5%, see Table 2) compared with 17.2 for the control. The combined polymer treatment (PEG 3400 + PTHF 250) did not significantly improve the stability toward UV-light (**d** in Fig. 1).

Figure 2 shows the rate of yellowing of the FWA-treated sheets. As can be seen in the figure, the addition of Phorwite UW Liquid did not significantly change the overall discoloration process; the brightness curves are similar in shape although shifted to a higher brightness level. There is, however, a retarding effect although the brightness losses are similar [this is because brightness is not linearly related to the chromophore content of the paper - a consequence of the Kubelka-Munk relationship, cf. Johnson (1989)]. Tinopal SFP did retard yellowing somewhat more efficiently than Phorwite UW Liquid due to its higher concentration of active fluorescent substance; a PC_2 value as low as 5.3 (calculated with the fluorescent component of the treated paper after 4 hours of irradiation) was obtained with the high application level (1.8%) (Table 2). It is, however, important to bear in mind that the visual appearance of an optical brightening agent treated paper is dependent on the closeness of match between the light source (UV/blue ratio of the light) employed for visual assessment and the light source (UV/blue ratio) and parameters [cut of filter(s), integrating sphere, and detector] of the fluorescent measurement instrument used. Care should therefore always be taken when optical properties of FWA-treated papers are discussed so that no misjudgments of the total appearance of the paper occur. The Technidyne Brightimeter (Model S-5) used in this investigation for optical measurements is equipped with a quartz tungsten halogen lamp and uses a cutoff filter that is absorbent up to 420 nm that completely excludes the brightening effect of the FWA (cf. Muller et al. 1993). The brightness value without the fluorescent component is given in Table 2, both before aging and after 4 hours of irradiation. It is evident that the addition of optical brightening agents has a real photostabilizating effect. This is most likely a result of their ability to absorb ultraviolet radiation and thereby protect the light-sensitive structures in lignin. On prolonged exposure, the fluorescent whitening agents lose their efficiency, an effect that can be seen as a reduction in the fluorescent component (ΔF in Table 2).

The influence of addition of Tinuvin 384 and HMB on the photoaging properties is shown in Fig. 3. Both of the UV absorbers retarded yellowing significantly. The brightness after 4 hours of irradiation was 65.0% (Tinuvin 384) and 67.6% (HMB) for the high charge level, which is more than 10 brightness units higher than for the control (54.6%). The observed photostabilization is probably an effect of a reduction in the ultraviolet light transmitted onto the pulp, although other possibilities such as radical scavenging and triplet quenching, in part, can explain the effectiveness of the examined UV-screens (Castellan et al. 1994; Noutary et al. 1994; Castellan et al. 1996; Cook, Ragauskas 1997). The radical scavenger tested (MESNA, Fig. 4) did not stabilize the high-brightness aspen CTMP, at least not for the tested application levels.

The total effect of addition of inhibitors on photoyellowing is best illustrated by the PC-number (cf. Table 2). The most effective additives in preserving a high final brightness of the treated paper, at moderate charge levels, are the FWAs and the UV-screens. However, the most important factor for the paper manufacturer (and the consumer) is that the paper has a stable brightness level, i.e., has a low PC_2-value (Table 2). In this sense, benzophenone and Tinopal SFP (charge level $\approx$ 1%) show the most promising results.

The effect of irradiation on the yellowing of acetylated high-brightness aspen CTMP

Table 3 shows the change in optical properties during acetylation. As can be seen, acetylation lowered the brightness considerably even at a low degree of derivatization. The large loss in brightness indicates that new chromophoric structures have been generated. This is contradictory to earlier reported results for hydrogen-peroxide-bleached high-yield pulps where acetylation for 10 minutes (100°C) lowered the brightness of a bleached spruce TMP (initial brightness 77%) with one brightness unit and a bleached aspen CTMP (brightness 80%) with 2 units (Paulsson et al. 1994). The corresponding value for the high-brightness CTMP used in this work was 5.8 brightness units. The decrease in brightness was manifested as a decrease in lightness (L^*) and an increase in yellowness (b^*), which increased the yellowish cast of the treated paper. The difference in the manufacturing process, i.e., the pretreatment step with hydrogen peroxide for the high-brightness CTMP, is one likely explanation for the altered response toward acetylation. Further experiments are, however, needed to fully elucidate this discrepancy.

The brightness change during irradiation of acetylated test sheets is shown in Fig. 5 and Table 4. It is evident that acetylation retards photoyellowing, although to a lesser extent than previously reported (Paulsson et al. 1995; Paulsson et al. 1996). The chemical pretreatment step generates not only structures that are detrimental during acetylation, but also light-sensitive structures that form colored chromophores during the accelerated irradiation conditions used (see below). However, most of the photostabilization achieved appears already after a short period of acetylation; only a moderate reduction in the PC_2-value is obtained at higher derivatization degrees (cf. Table 4). A reaction time of 5 minutes derivatized about 80% of the phenolic hydroxyl groups, which is in accordance with previously reported results (Paulsson et al. 1994).

The accelerated aging system used in this work uses UV-lamps ("blacklight") as a light source. These lamps emit light in a band between 300 and 420 nm (λ_{max} = 350 nm), i.e., the visible component of diffuse sunlight or office light is missing. This could be one explanation for the divergence in aging stability obtained for the two hardwood CTMPs. A forthcoming paper will discuss the effect of different light sources on the yellowing properties of unbleached and hydrogen-peroxide-bleached untreated and acetylated high-yield pulps.

The effect of irradiation on the yellowing of additive-impregnated, acetylated high-brightness aspen CTMP

Acetylated test sheets were impregnated with different classes of inhibitors, and the photoaging properties were determined. The results are summarized in Table 5 and Figs. 6 to 9. The two lowest acetylation levels (acetyl content of 4.1 and 6.0%) were chosen together with a low addition of inhibitor (between 0.7 and 4.1% depending on the additive used). This was done to see if an acceptable photostability could be obtained with a moderate use of chemicals. Most of the results presented in the table and figures are from the experiments with the higher acetylated

test sheets. The photoaging properties for the low acetylated sheets were, in general, the same, although shifted to a somewhat lower stability level (as indicated by the lower acetyl content), and will therefore not be discussed further.

A comparison of the PC_2-numbers for PEG 600- and PEG 3400-impregnated acetylated sheets indicated that both of the polyglycols were nearly equally effective in their ability to retard yellowing of acetylated handsheets (Table 5). Polytetrahydrofuran was more effective in preserving the brightness during irradiation as was the case when applied to unacetylated handsheets, whereas a combination of the two polyethers did not significantly improve the performance (**c** and **d** in Fig. 6). The final brightness (after 4 hours of irradiation) was 1 to 3 brightness units higher for the PEG-impregnated acetylated handsheets than for the acetylated sheets alone. The corresponding value for the PTHF-treated acetylated sheets was 3 to 6 units (cf. Table 4 and Table 5).

The photostabilizing effect of the two fluorescent whitening agents was small; the PC_2-values (4h irradiation) were in the same range as for acetylation alone, i.e., about 7.7 to 9.0 (Fig. 7 and Table 5). Furthermore, acetylation affected the performance of the FWAs negatively, which can be seen as a lower ΔF, i.e., a lower brightness on application. It is well-known that the brighter the pulp is (and the lower the yellow cast is), the better is the effect obtained with FWAs. Because acetylation both increased the yellowness (b^*) and decreased the brightness, optical brightening agents are not a good alternative to use in combination with the acetylated high-brightness CTMP used in this work.

As can be seen in Fig. 8, the combined treatment, acetylation and 2-hydroxybenzophenone (HMB) or benzotriazole (Tinuvin 384) derivatives, efficiently inhibited the light-induced yellowing even after long periods of irradiation. The final brightness after 4 hours of irradiation of the high charge level (2.8%) 2-hydroxy-4-methoxybenzophenone-treated sheets was 74.5%, which is about 19 brightness units higher than for the control (Table 5). This corresponds to a total photostability as high as 90% (calculated from the PC-number). The radical scavenger, 2-mercaptoethanesulfonic acid (MESNA), did not improve the photoaging properties of acetylated test sheets (Fig. 9).

In summary, the use of ultraviolet absorbing compounds in combination with chemical modification (e.g., acetylation) is a possible way to strongly retard the photoyellowing characteristics of high-brightness aspen CTMP.

Conclusions

This work demonstrates that the light-induced brightness reversion of high-brightness, hydrogen-peroxide-bleached aspen CTMP strongly can be retarded if a combination of chemical modification (e.g., acetylation) and ultraviolet-absorbing compounds is employed. This was achieved at a low degree of acetylation (acetyl content less than 5%) and with a low addition of UV-screen.

Fluorescent whitening agents provided a moderate photostabilization effect, but did not alter the general discoloration process. The effectiveness of the fluorescent whitening agents was strongly reduced on prolonged irradiation and when applied onto acetylated handsheets. Polytetrahydrofuran was more effective than the polyethylene glycols in hindering the light-induced discoloration both alone and in combination with acetylation.

The high-brightness aspen CTMP responded differently toward acetylation than previously examined unbleached and hydrogen-peroxide-bleached high-yield pulps. The brightness loss during reaction was higher (up to 10.6 brightness units depending on the degree of derivatization) and the inhibiting effect slightly lower than previously noted. The chemical pretreatment step with hydrogen-peroxide employed for the high-brightness pulp and the accelerated aging procedure used could possibly explain the divergence in obtained results. Experiments designed to clarify these differences in response toward acetylation are currently being conducted.

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Figure captions

Fig. 1. The change in TAPPI brightness after accelerated light-induced aging of untreated (□) and polyether-impregnated hydrogen-peroxide-bleached aspen CTMP. Abbreviations as in Table 1. Legends (application level): ***a****: (◊), 1.9%; (○), 4.0%; (Δ), 10.3%.* ***b****: (◊), 1.7%; (○), 3.8%; (Δ), 8.7%.* ***c****: (◊), 2.0%; (○), 3.4%; (Δ), 6.5%.* ***d****: (◊), 1.6%/1.6%; (○), 2.2%/2.2%; (Δ), 4.7%/4.7%.*

Fig. 2. The change in TAPPI brightness after accelerated light-induced aging of untreated (□) and fluorescent whitening agent-impregnated hydrogen-peroxide-bleached aspen CTMP. Abbreviation levels as in Table 1. Legends (application level): ***a****: (◊), 1.3%; (○), 2.1%; (Δ), 2.8%.* ***b****: (◊), 0.6%; (○), 1.1%; (Δ), 1.8%.*

Fig. 3. The change in TAPPI brightness after accelerated light-induced aging of untreated (□) and UV-screen-impregnated hydrogen-peroxide-bleached aspen CTMP. Abbreviations as in Table 1. Legends (application level): ***a****: (◊), 0.9%; (○), 1.2%; (Δ), 2.3%.* ***b****: (◊), 0.7%; (○), 1.5%; (Δ), 3.4%.*

Fig. 4. The change in TAPPI brightness after accelerated light-induced aging of untreated (□) and radical scavenger-impregnated hydrogen-peroxide-bleached aspen CTMP. Abbreviations as in Table 1. Legends (application level): (◊), 0.4%; (○), 0.8%; (Δ), 2.3%.

Fig. 5. The change in TAPPI brightness after accelerated light-induced aging of untreated (□) and acetylated hydrogen-peroxide-bleached aspen CTMP. Legends (acetyl content): (◊), 4.1%; (○), 6.0%; (Δ), 9.7%; (∇), 10.3%.

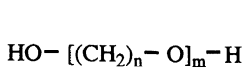
Fig. 6. The change in TAPPI brightness after accelerated light-induced aging of untreated (□) and polyether-impregnated, acetylated (acetyl content, 6.0%) hydrogen-peroxide-bleached aspen CTMP. Abbreviations as in Table 1. Legends (application level): ***a****: (◊), 0.0%; (○), 2.0%; (Δ), 4.1%.* ***b****: (◊), 0.0%; (○), 1.7%; (Δ), 3.2%.* ***c****: (◊), 0.0%; (○), 1.5%; (Δ), 3.5%.* ***d****: (◊), 0.0%; (○), 1.1%/1.1%; (Δ), 1.8%/1.8%.*

Fig. 7. The change in TAPPI brightness after accelerated light-induced aging of untreated (□) and fluorescent whitening agent-impregnated, acetylated (acetyl content, 6.0%) hydrogen-peroxide-bleached aspen CTMP. Abbreviations as in Table 1. Legends (application level): ***a****: (◊), 0.0%; (○), 0.7%; (Δ), 1.5%.* ***b****: (◊), 0.0%; (○), 0.7%; (Δ), 1.1%.*

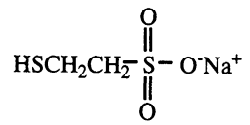
Fig. 8. The change in TAPPI brightness after accelerated light-induced aging of untreated (□) and UV-screen-impregnated, acetylated (acetyl content, 6.0%) hydrogen-peroxide-bleached aspen CTMP. Abbreviations as in Table 1. Legends (application level): ***a****: (◊), 0.0%; (○), 0.8%; (Δ), 1.3%.* ***b****: (◊), 0.0%; (○), 1.5%; (Δ), 2.8%.*

Fig. 9. The change in TAPPI brightness after accelerated light-induced aging of untreated (□) and radical scavenger-impregnated, acetylated (acetyl content, 6.0%) hydrogen-peroxide-bleached aspen CTMP. Abbreviations as in Table 1. Legends (application level): (◊), 0.0%; (○), 1.5%; (Δ), 2.2%.

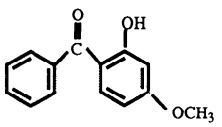
Appendix 1: Structures of the additives used



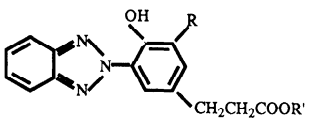
PEG 600: n = 2, m = 13
PEG 3400: n = 2, m = 77
PTHF 250: n = 4, m = 3



MESNA

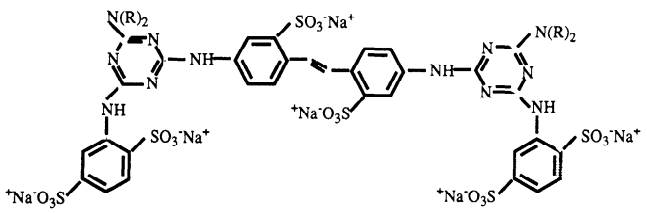


HMB



Tinuvin 384

R = $C(CH_3)_3$
R' = C7-9-branched alkyl esters



R = CH_2CH_3 **Tinopal SFP**
R = CH_2CH_2OH **Phorwite UW Liquid**

Table 1. Change in optical properties on impregnation of hydrogen-peroxide-bleached aspen CTMP with various classes of additives.

Additive	Charge level, %	TAPPI brightness, %	Δ TAPPI brightness, %	L*	a*	b*	PC_1-number[a]
(None)	----	83.2	0.0	95.2	-1.3	4.3	0.00
Polyethylene glycol 600 (PEG 600)	1.9	83.2	0.1	95.3	-1.1	4.5	-0.02
	4.0	83.2	0.0	95.2	-1.0	4.3	0.00
	10.3	83.4	0.3	95.3	-1.2	4.4	-0.07
Polyethylene glycol 3400 (PEG 3400)	1.7	83.3	0.4	95.3	-1.1	4.4	-0.08
	3.8	83.8	0.8	95.4	-1.2	4.3	-0.18
	8.7	83.5	0.7	95.3	-1.1	4.2	-0.16
Polytetrahydrofuran 250 (PTHF 250)	2.0	83.2	0.4	95.1	-1.4	4.2	-0.08
	3.4	84.0	1.0	95.5	-1.3	4.2	-0.21
	6.5	83.6	0.9	95.3	-1.1	4.2	-0.19
Polyethylene glycol 3400/ polytetrahydrofuran 250	1.6/1.6	83.5	0.2	95.2	-1.5	4.2	-0.05
	2.2/2.2	83.6	0.8	95.2	-1.5	4.1	-0.18
	4.7/4.7	83.7	0.9	95.3	-1.6	4.1	-0.19
Phorwite UW Liquid[b, c]	1.3	84.6 (82.6)	1.7	95.0	-1.1	2.9	-0.37
	2.1	87.5 (82.7)	4.3	95.2	-0.6	0.8	-0.81
	2.8	90.2 (82.0)	7.6	95.2	0.7	-1.4	-1.31
Tinopal SFP[c, d]	0.6	89.0 (82.6)	6.4	95.2	0.6	-0.5	-1.15
	1.1	91.2 (82.5)	8.1	95.4	0.9	-1.5	-1.29
	1.8	91.9 (82.4)	8.6	95.6	0.9	-1.3	-1.31
Tinuvin 384[e]	0.9	83.3	-0.3	95.4	-1.1	4.6	0.05
	1.2	83.1	-0.6	95.4	-1.2	4.8	0.14
	2.3	82.5	-1.0	95.3	-1.4	5.0	0.22
2-Hydroxy-4-methoxy-benzophenone (HMB)	0.7	82.6	-0.9	95.4	-1.9	5.3	0.20
	1.5	80.7	-3.3	95.2	-3.1	6.8	0.80
	3.4	78.4	-4.2	94.9	-3.3	8.1	1.15
2-Mercaptoethanesulfonic acid, monosodium salt (MESNA)	0.4	84.1	1.3	96.1	-0.9	5.2	-0.29
	0.8	84.2	1.5	96.0	-0.9	5.0	-0.32
	2.3	84.2	2.0	96.1	-0.9	5.0	-0.49

[a]The post color (PC_1) number at 457 nm (due to treatment with various additives) was calculated according to Giertz (1945).

[b]The active fluorescent component is 2,2'-[1,2-Ethenediylbis[(3-sulfo-4,1-phenylene)imino-[6-[bis(2-hydroxyethyl)amino]-1,3,5-triazine-4,2-diyl]imino]]bis-1,4-benzenedisulfonic acid, hexasodium salt.

[c]Brightness values without the fluorescent component are given within parentheses (measured according to TAPPI Test Method T 452 om-92).

[d]2,2'-[1,2-Ethenediylbis[(3-sulfo-4,1-phenylene)imino-[6-(diethylamino)-1,3,5-triazine-4,2-diyl]imino]]bis-1,4-benzenedisulfonic acid, hexasodium salt; sodium chloride.

[e]Benzotriazole derivative [3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxybenzenepropanoic acid, C7-9-branched alkyl esters].

Table 2. Change in optical properties during irradiation of hydrogen-peroxide-bleached aspen CTMP treated with various additives.

Additive[a]	Charge level, %	Initial TAPPI brightness, %	ΔF[b]	PC_2-number[c] 0.5 h	PC_2-number[c] 4 h	PC-number[d] 0.5 h	PC-number[d] 4 h	Final TAPPI[e] brightness, %	ΔF[b]	L*	a* 4h	b*
(None)	----	83.2		4.5	17.2	4.5	17.2	54.6		89.1	-2.0	18.8
PEG 600	1.9	83.2		3.9	14.6	3.9	14.6	57.0		89.8	-2.1	17.7
	4.0	83.2		3.9	13.0	3.9	13.0	58.5		90.4	-2.2	17.3
	10.3	83.4		3.2	9.7	3.1	9.6	62.4		91.6	-2.3	15.7
PEG 3400	1.7	83.3		4.3	15.2	4.2	15.1	56.4		89.7	-2.0	18.1
	3.8	83.8		4.1	13.2	3.9	13.1	58.4		90.3	-2.1	17.2
	8.7	83.5		3.5	12.1	3.3	12.0	59.5		90.7	-2.2	16.8
PTHF 250	2.0	83.2		3.7	11.9	3.6	11.9	59.7		90.6	-2.4	16.6
	3.4	84.0		3.9	11.9	3.7	11.7	59.9		90.6	-2.3	16.3
	6.5	83.6		3.1	10.2	2.9	10.0	61.8		91.2	-2.1	15.5
PEG 3400/PTHF 250	1.6/1.6	83.5		3.1	10.8	3.0	10.7	61.1		91.1	-2.7	16.1
	2.2/2.2	83.6		3.1	10.9	2.9	10.7	60.9		90.9	-2.9	15.9
	4.7/4.7	83.7		2.7	8.9	2.5	8.7	63.5		91.7	-2.9	14.8
Phorwite UW Liquid[f]	1.3	84.6 (82.6)	2.0	3.6	14.1	3.2	13.7	57.9 (57.5)	0.4	90.0	-2.5	17.4
	2.1	87.5 (82.7)	4.8	2.7	12.0	1.9	11.2	60.6 (59.3)	1.3	90.8	-2.6	16.0
	2.8	90.2 (82.0)	8.2	1.7	9.0	0.4	7.7	64.9 (61.8)	3.1	91.2	-1.7	12.6
Tinopal SFP[f]	0.6	89.0 (82.6)	6.4	2.0	11.4	0.8	10.2	61.4 (59.4)	2.0	90.3	-1.5	14.5
	1.1	91.2 (82.5)	8.7	1.2	7.1	-0.1	5.8	68.1 (63.9)	4.2	91.8	-1.4	10.5
	1.8	91.9 (82.4)	9.5	0.9	5.3	-0.4	4.0	71.6 (66.4)	5.2	92.3	-1.0	9.0
Tinuvin 384	0.9	83.3		2.4	10.7	2.5	10.8	61.2		90.9	-2.0	15.5
	1.2	83.1		2.1	9.0	2.3	9.1	63.2		91.5	-2.1	14.7
	2.3	82.5		1.7	7.6	1.9	7.8	65.0		91.9	-2.3	13.7
HMB	0.7	82.6		2.1	8.5	2.3	8.7	63.7		91.6	-2.7	14.7
	1.5	80.7		1.4	6.2	2.2	7.0	66.3		92.6	-3.7	14.1
	3.4	78.4		1.0	4.8	2.2	5.9	67.6		92.7	-3.8	13.4
MESNA	0.4	84.1		4.9	17.9	4.6	17.6	54.2		89.7	-1.1	20.3
	0.8	84.2		4.2	17.7	3.8	17.4	54.4		89.7	-1.3	20.1
	2.3	84.2		3.7	16.4	3.3	15.9	55.5		90.2	-1.5	19.9

[a] Abbreviations as in Table 1.

[b] The fluorescent component, ΔF = brightness measured without UV cutoff filter - brightness measured with UV cutoff filter.

[c] The post color (PC_2) number at 457 nm (due to irradiation) was calculated according to Giertz (1945).

[d] The post color (PC) number (at 457 nm) [due to treatment with various additives (PC_1) + irradiation (PC_2)] was calculated according to Giertz (1945).

[e] TAPPI brightness after 4 h irradiation.

[f] Brightness values without the fluorescent component are given within parentheses (measured according to TAPPI Test Method T 452 om-92).

Table 3. Change in optical properties on acetylation of hydrogen-peroxide-bleached aspen CTMP. Acetylation times (min) are given within parentheses.

Pulp		Acetyl content, % by mass	TAPPI brightness, %	L*	a*	b*	PC_1-number[a]
Control		0.6	84.3	95.8	-1.0	4.3	0.00
Acetylated	(5)[b]	4.1	80.9	95.3	-1.4	6.4	0.87
	(10)[b]	6.0	78.5	94.9	-1.3	7.6	1.56
	(10)[c]	9.7	74.3	93.7	-1.1	8.8	3.06
	(25)[b]	10.3	73.7	93.7	-1.1	9.3	3.31

[a]The post color (PC_1) number at 457 nm (due to acetylation) was calculated according to Giertz (1945).

[b]Acetylation temperature, 100 °C.

[c]Acetylation temperature, 110 °C.

Table 4. Change in optical properties during irradiation of hydrogen-peroxide-bleached aspen CTMP acetylated to various degrees. Acetylation times (min) are given within parentheses.

Pulp		Acetyl content % by mass	Initial TAPPI brightness, %	PC_2-number[a] 0.5 h	PC_2-number[a] 4 h	PC-number[b] 0.5 h	PC-number[b] 4 h	Final TAPPI[c] brightness, %	L*	a* 4 h	b*
Control		0.6	84.3	4.1	16.2	4.1	16.2	55.6	89.6	-2.1	18.7
Acetylated	(5)[d]	4.1	81.0	3.8	12.0	4.7	12.9	59.0	91.5	-1.8	18.8
	(10)[d]	6.0	78.6	3.0	9.3	4.5	10.8	61.2	91.9	-1.8	17.5
	(10)[e]	9.7	74.6	2.3	6.1	5.4	9.2	63.8	92.6	-1.9	16.2
	(25)[d]	10.3	73.7	2.0	5.0	5.3	8.3	64.5	92.8	-1.9	15.8

[a]The post color (PC_2) number at 457 nm (due to irradiation) was calculated according to Giertz (1945).

[b]The post color (PC) number at 457 nm [due to acetylation (PC_1) and irradiation (PC_2)] was calculated according to Giertz (1945).

[c]TAPPI brightness after 4 h irradiation.

[d]Acetylation temperature, 100 °C.

[e]Acetylation temperature, 110 °C.

Table 5. Change in optical properties during irradiation of additive-treated, acetylated hydrogen-peroxide-bleached aspen CTMP. The acetyl content (% by mass) was 6.0% unless stated otherwise.

Additive[a]	Charge level, %	Initial TAPPI brightness, %	ΔF[b]	PC_2-number[c] 0.5 h	PC_2-number[c] 4 h	PC-number[d] 0.5 h	PC-number[d] 4 h	Final TAPPI[e] brightness, %	ΔF[b]	L*	a* 4h	b*
(None)	----	84.3		4.1	16.2	4.1	16.2	55.6		89.6	-2.1	18.7
PEG 600	2.0	79.2		3.0	8.1	2.7	7.8	63.0		92.3	-1.8	16.5
	4.1	78.7		2.8	7.1	2.5	6.8	64.2		92.6	-2.0	15.8
PEG 3400	1.7	78.1		3.3	8.3	3.1	8.1	62.3		92.0	-1.7	16.5
	3.2	78.2		2.8	7.0	2.6	6.8	64.2		92.6	-1.9	15.9
PTHF 250	1.5	78.3		2.4	6.8	2.2	6.5	64.4		92.8	-1.8	16.1
	3.5	78.2		2.1	5.1	1.8	4.8	67.0		93.5	-2.0	15.0
PEG 3400/PTHF 250	1.1/1.1	77.5		2.4	6.7	2.2	6.5	64.2		92.8	-1.8	16.2
	1.8/1.8	78.7		2.2	5.6	1.9	5.2	66.4		93.5	-2.0	15.5
Phorwite UW Liquid[f]	0.7	78.9 (78.0)	0.9	2.9	8.6	2.5	8.2	62.2 (62.1)	0.1	92.4	-1.6	17.6
	1.5	83.4 (78.9)	4.5	2.6	9.0	1.6	8.0	63.2 (62.1)	0.1	92.3	-1.2	16.2
Tinopal SFP[f]	0.7	79.4 (77.6)	1.8	3.0	8.8	2.3	8.1	62.3 (62.0)	0.3	92.4	-1.6	17.3
	1.1	82.3 (77.6)	4.7	2.1	7.7	0.6	6.2	64.8 (63.0)	1.8	92.7	-1.3	15.3
Tinuvin 384	0.8	78.1		2.1	6.5	1.8	6.3	64.8		92.8	-1.7	15.6
	1.3	78.6		1.7	5.4	1.0	4.7	66.6		93.2	-1.6	14.6
HMB	1.6[g]	80.8		1.9	7.1	1.8	7.0	65.0		92.7	-1.7	15.4
	2.7[g]	80.8		0.7	2.2	0.6	2.0	74.3		94.5	-1.3	10.2
	1.5	78.1		1.9	5.7	1.7	5.4	66.0		93.1	-1.6	15.0
	2.8	79.2		0.5	1.6	0.5	1.5	74.5		94.7	-1.3	10.4
MESNA	1.5	77.5		2.9	9.8	2.7	9.5	60.3		92.0	-1.7	18.4
	2.2	80.3		3.0	10.7	2.6	10.3	60.2		92.0	-2.0	18.5

[a] Abbreviations as in Table 1.

[b] The fluorescent component, ΔF = brightness measured without UV cutoff filter - brightness measured with UV cutoff filter.

[c] The post color (PC_2) number at 457 nm (due to irradiation) was calculated according to Giertz (1945).

[d] The post color (PC) number (at 457 nm) [due to treatment with various additives and acetylation (PC_1) + irradiation (PC_2)] was calculated according to Giertz (1945).

[e] TAPPI brightness after 4 h irradiation.

[f] Brightness values without the fluorescent component are given within parentheses (measured according to TAPPI Test Method T 452 om-92).

[g] Acetyl content, 4.1%.

Figure 1

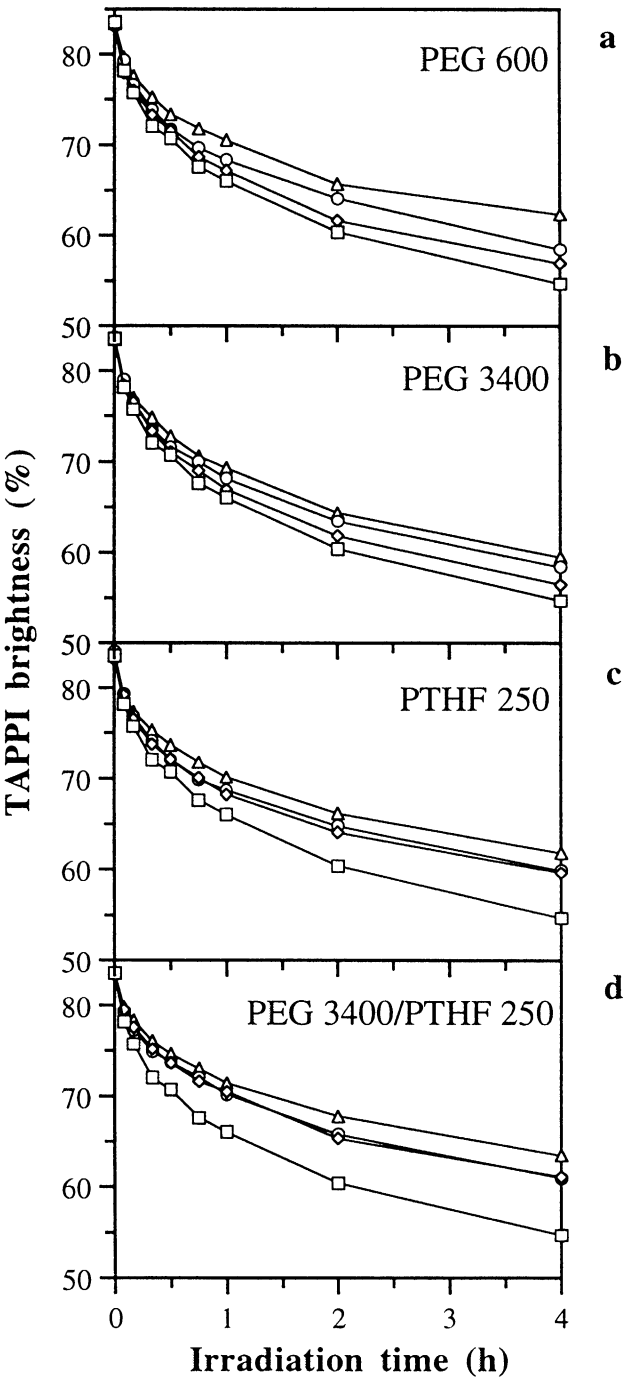

PEG 600
a
PEG 3400
b
PTHF 250
c
PEG 3400/PTHF 250
d
TAPPI brightness (%)
80
70
60
50
0
1
2
3
4
Irradiation time (h)

Figure 2

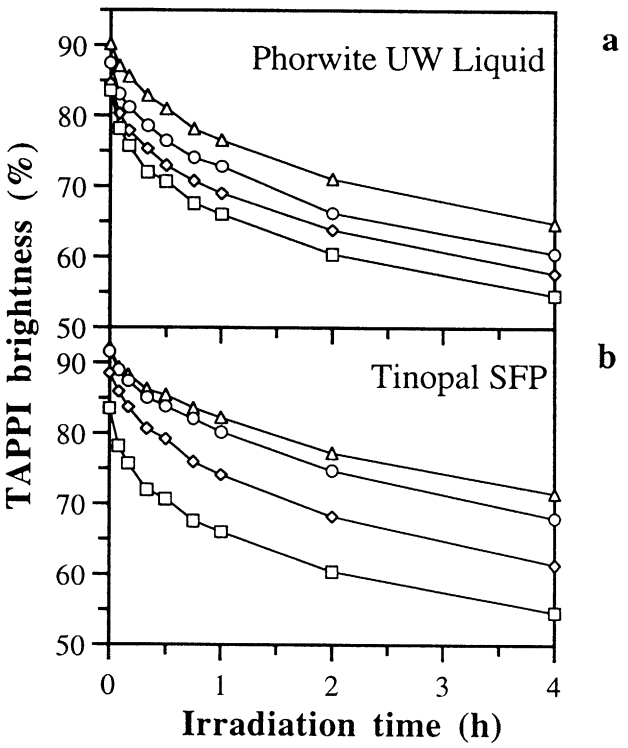

Phorwite UW Liquid
a
Tinopal SFP
b
TAPPI brightness (%)
90
80
70
60
50
0
1
2
3
4
Irradiation time (h)

Figure 3

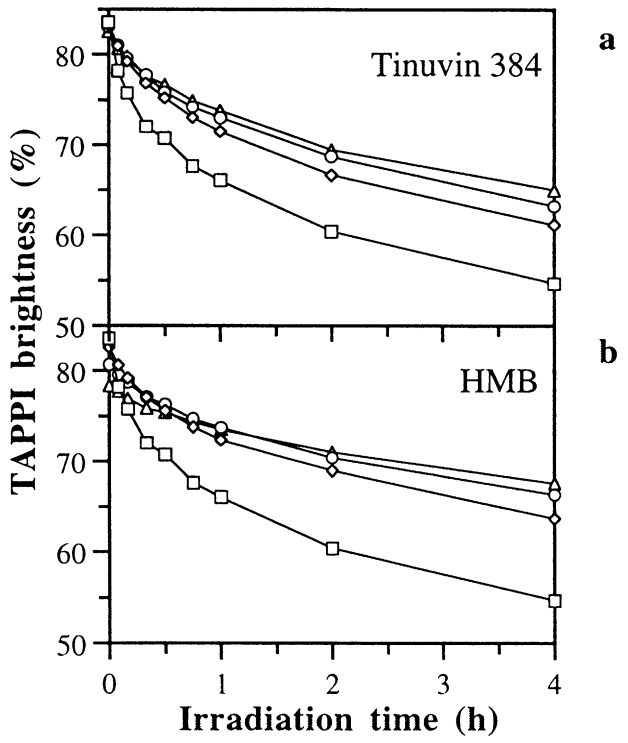

Tinuvin 384
a
HMB
b
TAPPI brightness (%)
80
70
60
50
80
70
60
50
0
1
2
3
4
Irradiation time (h)

Figure 4

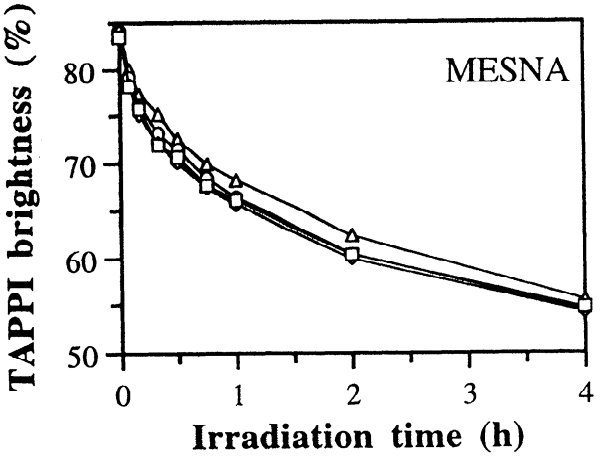


Figure 5

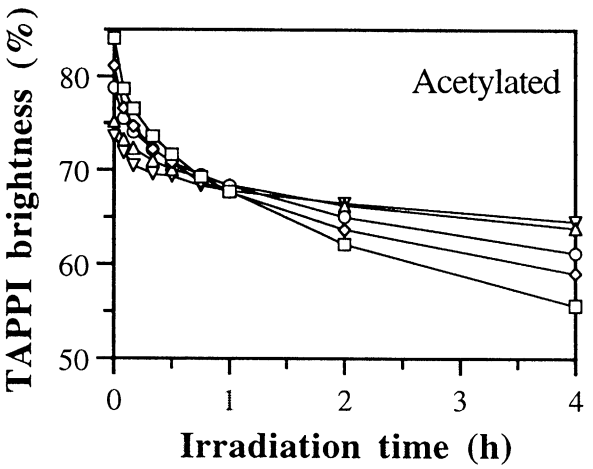

TAPPI brightness (%)
80
70
60
50
0
1
2
3
4
Irradiation time (h)
Acetylated

Figure 6

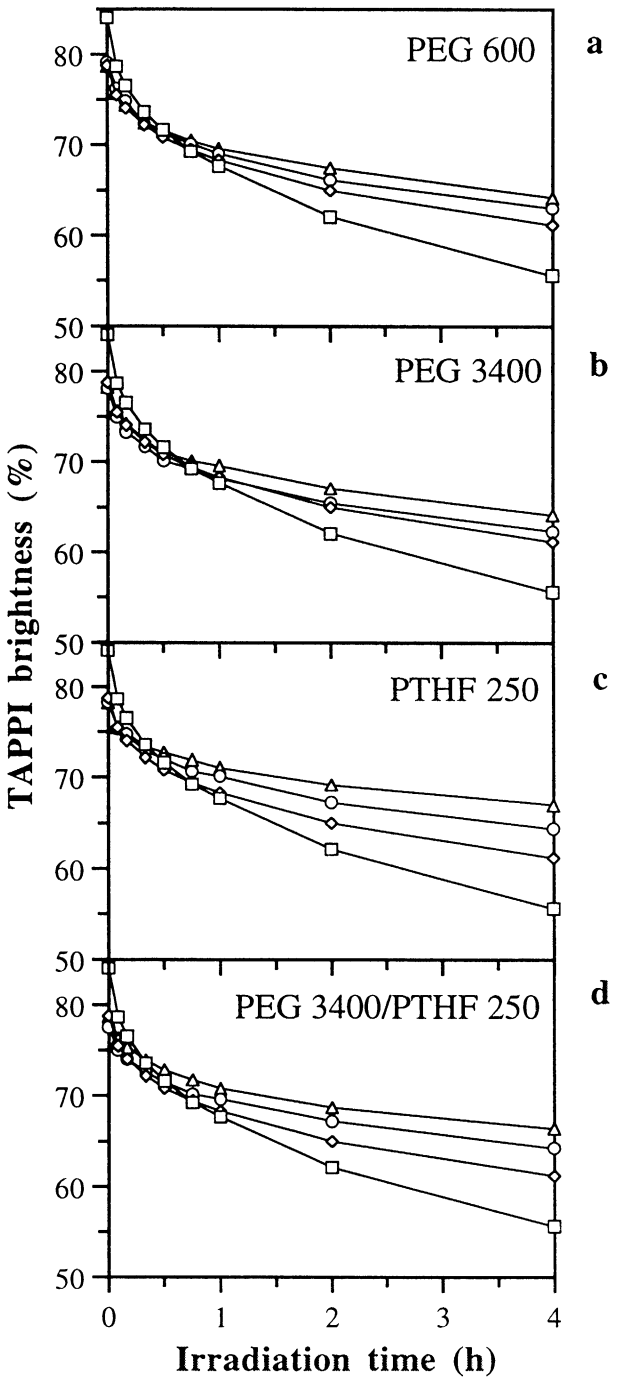

PEG 600
a
PEG 3400
b
PTHF 250
c
PEG 3400/PTHF 250
d
TAPPI brightness (%)
80
70
60
50
0
1
2
3
4
Irradiation time (h)

Figure 7

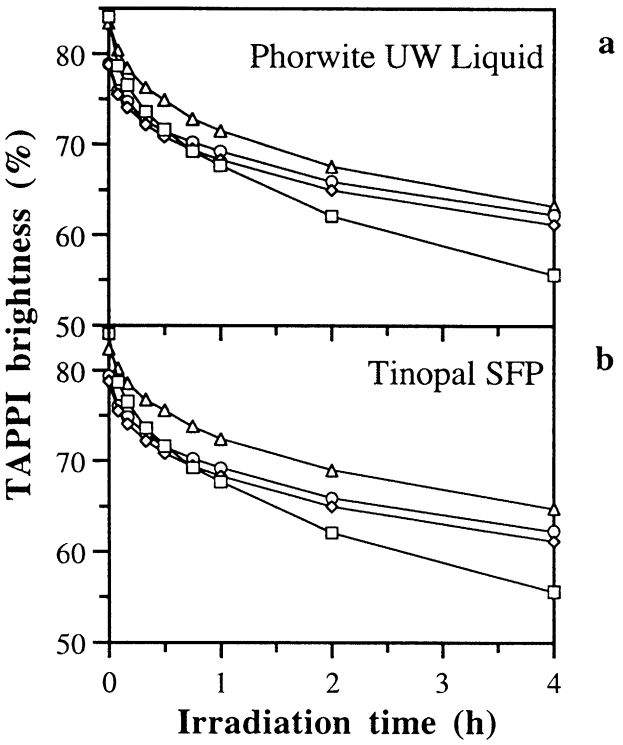

Phorwite UW Liquid
a
Tinopal SFP
b
TAPPI brightness (%)
80
70
60
50
80
70
60
50
0
1
2
3
4
Irradiation time (h)

Figure 8

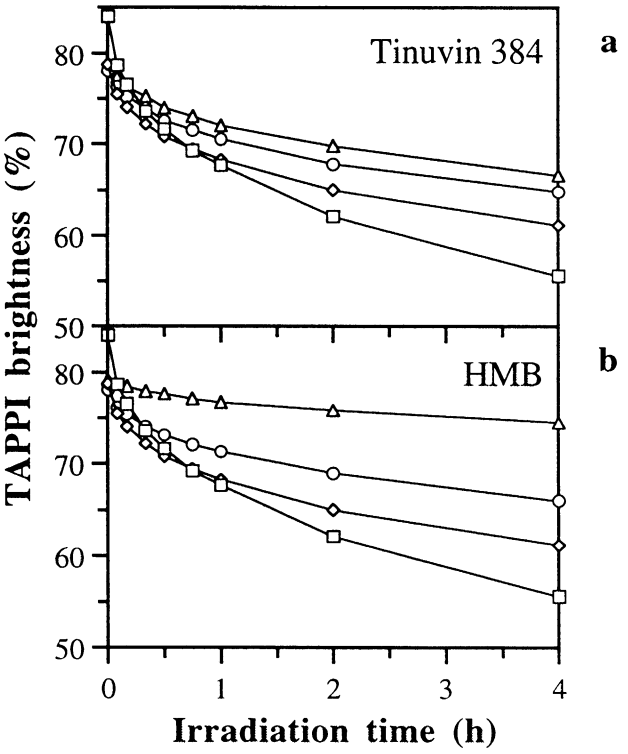
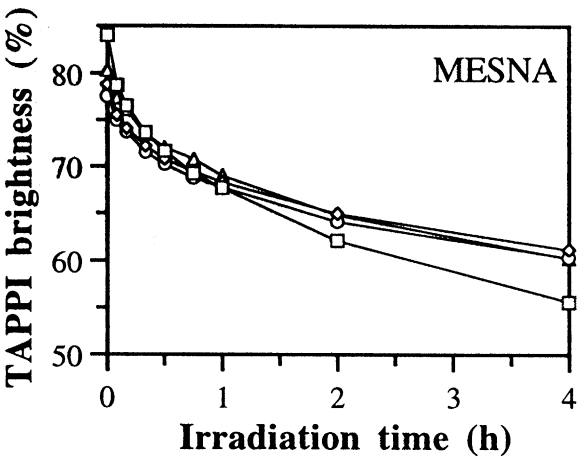

Tinuvin 384
a
HMB
b
TAPPI brightness (%)
80
70
60
50
0
1
2
3
4
Irradiation time (h)

Figure 9



Chemical modification of lignin-rich paper

Part 8. Effect of light source on the accelerated light-induced yellowing of untreated and acetylated high-yield pulps

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Keywords: Acetylation, Thermomechanical pulp, Chemithermomechanical pulp, Yellowing, Photobleaching, Inhibition, Light source, Hydrogen-peroxide-bleached, Ultraviolet absorbers

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SUMMARY: The effect of three different irradiation sources (e.g., ultraviolet "blacklight" fluorescent lamps, UV/VIS-fluorescent lamps, and a xenon lamp) on the photoyellowing properties of dithionite-bleached and hydrogen-peroxide-bleached spruce thermomechanical pulp (TMP) and hydrogen-peroxide-bleached spruce and aspen chemithermomechanical pulp (CTMP) has been examined. The aging response of additive-treated (e.g., UV-screen) and/or chemical-modified (acetylated), high-yield pulps toward the tested light sources is also highlighted.

The order of light-induced discoloration, of the different high-yield pulps examined, was determined to be: hydrogen-peroxide-bleached spruce TMP>hydrogen-peroxide-bleached spruce CTMP>dithionite-bleached spruce TMP>>hydrogen-peroxide-bleached aspen CTMP (pretreated with hydrogen peroxide). The spectral distribution of the tested light sources did only marginally alter the aging response of the unmodified, dithionite-bleached, and hydrogen-peroxide-bleached spruce pulps, whereas the high-brightness aspen CTMP showed some variation in the degree of brightness reversion. The acetylated and UV-screen impregnated pulps were, however, strongly dependent on the light source used, which emphasizes the importance of developing a standard method for accelerating testing and measurements of yellowing of lignin-containing materials that could be generally accepted by the research community.

The improved stability toward light, achieved by acetylation of high-yield pulps, is not only a consequence of retarding the color-forming reactions, but also to some degree an effect of promoting photobleaching reactions, both for nonirradiated and preyellowed pulps.

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The use of mechanical and chemimechanical pulps as constituent in higher grades of printing paper is severely restricted by the rapid color reversion (yellowing) that occurs upon exposure to daylight or indoor illumination. This phenomenon has been attributed to a light-induced oxidation of the lignin present in the pulp. Extensive and comprehensive research, performed during the last decade, has given not only new information about the photochemical reactions causing yellowing, but also information on the potential photostabilizing methods, although no single approach so far has become technically or economically feasible to meet all the needs of the paper industry. Heitner and Schmidt (1991) and Leary (1994) have summarized current knowledge in this field in two comprehensive literature reviews (cf. also Heitner 1993).

The photochemical changes that occur during the irradiation of lignin-rich pulps do not only involve discoloration reactions. Several researchers have reported a photobleaching effect when pulps were irradiated at longer wavelengths. If the color-forming reactions could be eliminated or slowed down, the bleaching reactions would be predominate and result in a brightness increase for high-yield pulps when irradiated in daylight. However, the darkening reactions normally dominate over the brightening reactions, and the net result is a discoloration of the lignin-rich material. The photoyellowing-photobleaching phenomenon has been observed in several investigations. Nolan et al. (1945) reported that the transition between photoyellowing and photobleaching, during irradiation of groundwood pulp (GWP), occurred at 385 nm. UV radiation of wavelengths 290 to 390 nm discolored unbleached and bleached spruce GWP, whereas light in the 420-470 nm range had a photobleaching effect (Andtbacka et al. 1989). It was further noted that the discoloration of the irradiated samples continued during storage in the dark. The most severe brightness loss was shown by the samples irradiated at lower wavelengths. Forsskåhl and Janson (1991) reported that unbleached and bleached chemimechanical pulp responded similarly toward irradiation at selected wavelengths between 280 and 600 nm. The strongest discoloration was observed on irradiation at 310-320 nm (cf. Forsskåhl, Tylli 1993). Forsskåhl and Tylli (1993) reported that the degrees of both photoyellowing and photobleaching were linearly dependent on light intensity. Andrady et al. (1991) used monochromatic radiation in the range of 260-600 nm and found that TMP-based newsprint was discolored on irradiation at short wavelengths in this interval. The transition from yellowing to bleaching was observed between 340 and 400 nm. In a continuation of this work, Andrady and Searle (1995) found that newsprint exposed to polychromatic radiation (similar to terrestrial sunlight) showed the largest amount of yellowing when subjected to irradiation in the wavelength region of 330-385 nm (UV-A region). This means that the wavelengths transmitted through window glass can still cause considerable amounts of yellowing in high-yield paper.

The intensity of sunlight varies with wavelength and passes through a maximum at approximately 470 nm. Most of the ultraviolet component of sunlight that reaches the earth's surface has wavelengths between 293 and 400 nm (Hirt et al. 1960). The total energy below 300 nm is very small, whereas the radiation energy between 300 and 350 nm is approximately one-third of that between 350 and 400 nm. Furthermore, the proportion below 350 nm is reduced indoors because of absorption by window glass. Lignin is a very efficient absorber of both UV radiation (due to its aromatic nature) and visible light, in contrast to cellulose, hemicelluloses, and extractives that have only some absorption in this region (λ>300 nm). This means that most of the absorption in lignocellulosic materials takes place in the lignin constituent. The important region of the sunlight spectrum is that between 300 and 550 nm, because the intensity of the sunlight below 300 nm is low, and the photoactive functional groups in lignin have their absorption maxima in this region (cf. Gratzl 1985).

No standard procedure has been established for the study of the light-induced yellowing of lignocellulosic materials. This complicates the interpretation of the results reported by different researchers. Differences in exposure conditions (humidity, temperature, etc.), light source (light intensity, spectral distribution, etc.), exposure time, grammage of the exposed sample, and the procedure chosen to measure and report the color reversion quantitatively greatly influence the experiments. The development of an accelerated reproducible testing method that could be generally accepted is therefore of considerable importance. (Although accelerated tests give rapid and reproducible testing conditions, subtle effects may be lost due to the high light intensity used.)

When lignocellulosic materials are exposed to light, the brightness reversion is primarily dependent on the wavelength and intensity distribution of the light source used, and it is therefore important to find a light source that simulates the solar spectrum or office illumination as close as possible. Several types of light sources have been used in accelerated tests, including xenon lamps, medium-pressure mercury lamps ("blacklights"), carbon-arc lamps, and sun lamps. Of these, the xenon lamp (used with borosilicate filters to eliminate light below 300 nm) provides a close match to the spectral energy distribution of natural daylight (cf. Hirt et al. 1960; Johnson 1989; Bailey, Lamont 1993).

The present paper describes the effect of irradiation sources with different wavelength distributions on the accelerated light-induced yellowing of untreated and acetylated and/or UV-screen-impregnated high-yield pulps. The effect of sequential irradiation of high-brightness aspen CTMP with different light sources is also discussed.

Experimental

Pulps and paper samples. Commercially produced dithionite-bleached and hydrogen-peroxide-bleached spruce (*Picea abies*) TMP together with hydrogen-peroxide-bleached spruce (*Picea abies*) and aspen (*Populus tremuloides*) CTMP were used as received for the studies described in this paper. The pulps were obtained as dried samples. The high-brightness hardwood CTMP was manufactured employing hydrogen peroxide both as a chemical pretreatment and as a bleaching stage. Handsheets (60 $g \cdot m^{-2}$) were prepared according to TAPPI Test Method T 205 om-88. The paper sheets were then conditioned at 23°C and 50% r.h. according to TAPPI Test Method T 402 om-88 before further treatment.

Solvents and photostabilizing additives. The solvents and the ultraviolet-absorbing additives [2-hydroxy-4-methoxybenzophenone (HMB) and Tinuvin 384 (3-(2H-benzotriazol-2-yl)-5-(1,1-dimethylethyl)-4-hydroxybenzenepropanoic acid, C7-9-branched alkyl esters, a benzotriazole derivative supplied by Ciba-Geigy Corporation)] were commercial products and were used as received.

Acetylation procedure. The handsheets [cut into strips (30 x 75 mm)] were acetylated (at 100°C or 110°C) according to the procedure described by Paulsson et al. (1994).

Impregnation procedure. Weighted amounts of ultraviolet-absorbing additives were dissolved in methanol (HMB) or acetone (Tinuvin 384) and sprayed onto handsheets. All experiments were replicated a minimum of two times.

Analyses. The acetyl content was calculated from the amount of acetate liberated after saponification with sodium hydroxide as previously described in Paulsson et al. (1996a). The acetyl content is given as a percentage of the dry weight of the paper. The amount of photostabilizing additive applied onto the handsheets was determined by weighing the handsheets prior to addition

and after reequilibrating of the treated handsheets (at 23°C and 50% r.h.). The addition level is given as a percentage of the conditioned weight of the paper.

Accelerated light-induced yellowing. The paper samples were subjected to an accelerated photoyellowing in a Rayonet photochemical reactor (Model RPR 100, The Southern New England Ultraviolet Company, Branford, CT, USA) equipped with eight RPR 3500Å UV-fluorescent lamps ("blacklight," The Southern New England Ultraviolet Company) or eight RPR 5750Å UV/VIS-fluorescent lamps (The Southern New England Ultraviolet Company) and a merry-go-round apparatus for uniform irradiation. The temperature was kept close to room temperature by a cooling fan (to minimize heating of the sample). Accelerating reversion studies were also conducted with a SUNTEST CPS (Heraeus HANAU, Hanau, Ger.) light-aging tester equipped with a xenon burner and filters (ultraviolet and window-glass), which eliminate radiation of wavelengths below 310 nm. The spectral distribution of the transmitted light was similar to that of average indoor daylight. The temperature was kept close to room temperature by a cooling fan. The irradiance was controlled by an optical sensor that compensates for possible main voltage fluctuations and burner aging. Untreated paper sheets were used in all radiation experiments as controls.

Optical measurements. TAPPI brightness and color changes according to the CIELAB color scale (L^*-, a^*-, b^*-values) were measured using a Technidyne Brightimeter (Model S-5) according to TAPPI Test Method T 452 om-92 and TAPPI Test Method T 524 om-94, respectively. The reflectance of a single sheet of paper (60 $g \cdot m^{-2}$) over a completely black, nonreflecting surface (over a hollow black body, reflectance <0.5%) and the reflectance over a stack of paper (high enough as to inhibit any transparence of light) were recorded. The specific light scattering coefficient (s, at 457 nm) was then calculated using the Kubelka-Munk theory. Optical properties of the SUNTEST CPS irradiated handsheets were measured using an Elrepho 2000 spectrophotometer. The post color (PC) number (at 457 nm, according to Giertz 1945) was calculated for the treatment with ultraviolet absorbing additive and/or acetylation (PC_1) and for the light-induced reversion (PC_2) (cf. Janson, Forsskåhl 1989). The sum of PC_1 and PC_2 represents the total effect of the treatment: $PC = PC_1 + PC_2$. The change in specific light-absorption coefficient (Δk, at 457 nm) during irradiation was calculated from the PC_2-value with the assumption of constant light scattering according to Johnson (1989).

Results and discussion

Light sources and measurements of the rate of yellowing

To assess the importance of the wavelength distribution of irradiation sources used for accelerated reversion tests, a series of handsheets made from untreated and acetylated high-yield pulps were irradiated with three different light sources, and the optical properties were monitored. The light sources chosen were ultraviolet fluorescent lamps ("blacklight," RPR 3500Å), UV/VIS-fluorescent lamps (RPR 5750Å), and a xenon burner, i.e., commonly used irradiation sources in many light-induced aging equipments. The UV-fluorescent lamps emit light in a band between 300 and 420 nm (approximately Gaussian spectral distribution, λ_{max} = 350 nm), i.e., the visible component of diffuse sunlight or office light is practically missing. The UV-fluorescent lamps give an assessment of the UV light-aging properties and could be useful when complications from other wavelengths are not desirable. The UV/VIS-fluorescent lamps emit light in the ultraviolet and visible range (from about 350 to 700 nm, λ_{max} = 575 nm) and have a comparatively close match to the conventional standard "cool white" fluorescent color used in many commercial lighting

installations. The energy distribution is enriched at 575 nm, i.e., most of the light is emitted in the visible part of the spectrum. The spectral distribution of the transmitted light from the xenon lamp (nominal rating of xenon burner, 1.1 kW) and filter combinations used was similar to that of average indoor daylight. The temperatures during irradiation were 29°C, 27°C, and 30°C for the UV-fluorescent lamps, UV/VIS-fluorescent lamps, and xenon lamp, respectively. Figures 1a-c summarize the spectral distribution of the three light sources, as received from the manufacturers. The spectral distribution of standard "cool white" fluorescent color (Waymouth 1992) and natural daylight (Merrigan 1975) is given, as a comparison, in Figs. 1b (broken line) and 1c (dotted line), respectively. The use of controls in each irradiation experiment and the exchange of UV/VIS-fluorescent lamps between aging series were done to monitor and minimize the effects of aging of the light sources studied.

The yellow color generated during the irradiation of high-yield pulps is caused by the formation of chromophores absorbing in the blue region of the spectrum. The changes in optical properties that occur can be characterized in several ways. One possibility is to express the degree of yellowing as the post color (PC) number (often given at 457 nm). The Kubelka-Munk equation is used to calculate $k \cdot s^{-1}$ according to Eq. [1] (Giertz 1945). In this formula, R_∞ is the reflectance of an optically thick (opaque) sheet. The PC-number is then calculated according to Eq. [2] where t is the irradiation time, k the specific light absorption coefficient, and s the specific light scattering coefficient.

$$k \cdot s^{-1} = [(1-R_\infty)^2 \cdot (2 \cdot R_\infty)^{-1}] \quad [1]$$

$$\text{PC-number} = 100 \cdot [(k \cdot s^{-1})_t - (k \cdot s^{-1})_{t=0}] \quad [2]$$

$$\Delta k = s_0 \cdot \text{PC-number}/100 \quad [3]$$

Because the light-induced photodegradation is most pronounced at the surface, the distribution of chromophores formed is not homogenous throughout the paper cross section (cf. Eriksson et al. 1988; Johnson 1989; Luo, Göttsching 1991; Forsskåhl et al. 1995a, b). The use of the Kubelka-Munk function is restricted because it is based on the assumption that the sample is homogenous. Furthermore, the post color number cannot compensate for large differences in light scattering when two samples with different s-values are compared. The inhomogeneity in chromophore distribution in the irradiated paper samples can be overcome by using thin sheets (grammage of approximately 10 $g \cdot m^{-2}$) because they are illuminated almost evenly throughout their thicknesses (Heitner, Min 1987; Schmidt, Heitner 1993). Because the formation, i.e., homogeneity regarding fibers, fines, fillers, etc., required by the Kubelka-Munk theory could not be fulfilled with such a low grammage, a grammage of 30-40 $g \cdot m^{-2}$ for high-yield pulps is recommended to minimize the errors caused by nonuniform formation (Lejong et al. 1987). The light absorption coefficient (k) of a sheet of paper is a parameter that is linear with respect to the chromophore content of the pulp, i.e., the brightness reversion can be expressed as the change in the light absorption coefficient. The inhomogeneity of the irradiated sample is, however, still a problem. A closer description of the change in color can be obtained from the L^*-, a^*-, and b^*-values according to the CIELAB color system. Measurement of the brightness loss is a convenient and fast method, but it can only be used to compare samples with the same initial brightness (a consequence of the Kubelka-Munk

relationship). The brightness is, however, of the utmost importance, because the PC-number gives information only about the changes that occur during irradiation (modification, etc.) and not about the absolute values reached after treatment. Furthermore, the brightness concept is in general use, i.e., both the researcher and the paper manufacturer can evaluate the effects of a light-stabilizing treatment.

In this work, the optical properties were measured on 60 $g \cdot m^{-2}$ paper sheets. The PC-number was then calculated according to equations [1] and [2] and the change in light absorption coefficient (Δk) according to equation [3] (based on the assumption of constant light scattering, s_0) according to Johnson (1989). Although the post color number is not an exact tool for kinetic studies, it gives an adequate approximation of the degree of yellowing under the different aging conditions studied. Furthermore, color measurements (i.e., L^*-, a^*-, and b^*-values) were monitored in some cases.

Optical properties of irradiated, unacetylated high-yield pulps

Table 1 summarizes the optical properties of unirradiated, unacetylated, and acetylated high-yield pulps. The pulps chosen for this study were a dithionite-bleached spruce TMP, hydrogen-peroxide-bleached spruce TMP and CTMP, and a hydrogen-peroxide-bleached aspen CTMP. The initial TAPPI brightnesses of the examined pulps were in the range between 65.7 and 84.3%, i.e., representing pulps with a wide range of initial chromophore contents.

Figures 2a-c and Table 2 show the effect of different light sources on the photoyellowing of dithionite-bleached and hydrogen-peroxide-bleached high-yield pulps. The dithionite-bleached spruce TMP was used as a control to determine the different periods of irradiation that were needed to obtain an approximately equivalent degree of light-induced reversion under the test conditions used. The comparison was made at 4, 216 (9 days), and 40 hours for the UV-fluorescent lamps, UV/VIS-fluorescent lamps, and xenon burner aged sheets, respectively. As can be seen in Figs. 2a and c, the yellowing of the UV-fluorescent lamps and xenon lamp irradiated sheets is characterized by a rapid initial phase that is followed by a slower phase. This is the general behavior of the discoloration process that has been reported by several researchers (Lewis et al. 1945; Francis et al. 1991; Ek 1992; Paulsson et al. 1996a). When the UV/VIS-fluorescent lamps were used as an irradiation source, the initial rapid phase was less pronounced, resulting in flatter brightness curves, especially for the high-brightness aspen CTMP (Fig. 2b). It is also evident that the degree of yellowing was somewhat more pronounced (larger Δk) for the hydrogen-peroxide-bleached spruce TMP and CTMP than for the dithionite-bleached spruce TMP (cf. Gellerstedt et al. 1983; Francis et al. 1991; Paulsson et al. 1996a). The Δk-values obtained were in the ranges 10-11 and 11-13 for the dithionite-bleached and hydrogen-peroxide-bleached pulps, respectively (Table 2). Furthermore, the bleached spruce CTMP was somewhat more stable than the bleached spruce TMP, as reported previously (Heitner, Min 1987; Johnson 1989; Schmidt, Heitner 1995). For practical purposes, however, the decrease in brightness is sufficient to cause a visible discoloration in a short period of time that limits the field of application for all of the softwood pulps tested.

Hardwood pulps have been reported to be more resistant toward light-induced aging than softwood pulps (Janson, Forsskåhl 1989; Johnson 1989; cf. Forsskåhl, Janson 1992). The rate of light-induced chromophore formation was significantly lower for the aspen CTMP compared with the other pulps examined in this investigation, and the variation in obtained aging results, between the different exposure techniques used, was larger. The change in light absorption coefficient (Δk) was between 2.7 and 6.2, i.e., ca. 40 to 75% lower than that for the softwood pulps (cf. Table 2).

In conclusion, with the exception of the high-brightness aspen CTMP, the different irradiation sources gave comparable aging results for all of the unmodified, bleached softwood pulps tested. The spectral distribution of the light sources did only marginally alter the photoyellowing characteristics of the examined softwood pulps.

Optical properties of irradiated, acetylated high-yield pulps

To establish if chemical modification (e.g., acetylation) of the pulps altered the aging response toward the tested irradiation sources, a series of test sheets were acetylated to various degrees. As can be seen in Table 1, the acetylation treatment resulted in a small brightness gain for the dithionite-bleached TMP (about 2 brightness units) and a small brightness loss for the hydrogen-peroxide-bleached spruce pulps (about 2.5 brightness units). The brightness loss for the hydrogen-peroxide-pretreated high-brightness aspen CTMP was more severe; an acetylation time of 25 minutes resulted in a brightness loss of more than 10 brightness units. The change in optical properties was manifested as an increase in the lightness (L^*) and a decrease in the yellowness (b^*) for the dithionite-bleached TMP, whereas the opposite was true for the hydrogen-peroxide-bleached pulps. In all cases, the change in a^*-value (green-red color vector in the three-dimensional color scale) was small. These findings agree well with results from earlier investigations (Paulsson et al. 1994; Paulsson, Ragauskas 1997).

As can be seen in Figs. 3 to 6 and Table 2, acetylation strongly inhibited the photoyellowing as previously reported (Paulsson et al. 1995; Paulsson et al. 1996a). Figure 3 illustrates the effect of light source on the yellowing properties of acetylated, dithionite-bleached TMP sheets. When irradiated with the UV/VIS-fluorescent lamps or xenon lamp, a photobleaching of the acetylated sheets took place. The effect was more pronounced for the UV/VIS-fluorescent lamps then for the xenon lamp (only a small initial brightness increase). As expected, the most severe yellowing (no photobleaching) was observed when the TMP sheets were irradiated with the UV-lamps (emit almost no light in the visible range). The PC_2-values after irradiation were -0.5 (UV/VIS-fluorescent lamps, i.e., negative sign indicates that the paper still is brighter than before irradiation), 5.5 (xenon lamp), and 9.3 (UV-fluorescent lamps) for the high acetylated TMP, see Table 2. This corresponds to a difference in brightness of more than 12 units after irradiation.

The change in brightness for the two acetylated hydrogen-peroxide-bleached spruce pulps is shown in Fig. 4 (TMP) and Fig. 5 (CTMP). Generally, the effect of the different irradiation sources was the same as for the unbleached TMP, although the photobleaching effect was smaller and obtained only for the pulps irradiated with the UV/VIS-fluorescent lamps. The difference in reverted brightness was about 11 brightness units for the low acetylated pulps (acetyl content of 3.5 to 4.6%) and more than 14 units for the high acetylated pulps (acetyl content, 6.7-9.4%) (Table 2).

The degree of reversion caused by the different light sources was in the order UV->xenon>> UV/VIS-fluorescent for the acetylated aspen CTMP (Fig. 6), i.e., the same order as for the other acetylated pulps. The UV/VIS-fluorescent lamps induced a rapid and strong photobleaching of the acetylated samples. The TAPPI brightness was ca. 82% after 24 hours of irradiation for all of the acetylated samples, which corresponds to a brightness gain of 1 to 8 brightness units depending on the derivatization degree studied. Thus, most of the colored substances formed on acetylation of hydrogen-peroxide-pretreated aspen CTMP can easily be converted to colorless structures during irradiation with visible light.

The photobleaching (a decrease in light absorption at $\lambda_{max} \approx 360$ nm) observed on irradiation of MWL and high-yield pulps has been attributed to the photooxidation of coniferaldehyde end groups

in lignin to produce vanillin-type end groups (Wang et al. 1993; Wang et al. 1995). Furthermore, the dissimilarities in the absorption difference spectra of peroxide-bleached softwood TMP and peroxide-bleached softwood CTMP have been explained in terms of coniferaldehyde photobleaching (Schmidt, Heitner 1995). It is also possible that quinonoid structures, absorbing in the blue-green region of the spectrum, photochemically convert to colorless structures (for general comments on light-induced reactions of quinones, cf. Bruce 1967; Bruce 1974). This has been demonstrated in the case of methoxy-*p*-benzoquinone incorporated in a solid carbohydrate matrix (i.e., 2-hydroxypropylcellulose); the photoreduction to methoxy-hydroquinone was a rapid process, whereas the photooxidation of the hydroquinone was comparatively slow (Castellan et al. 1993). Ragauskas (1993) reported that simple *para*- and *ortho*-quinones, impregnated onto cellulose sheets, did not in general cause any further darkening during irradiation (photolyzed with a xenon lamp). Several of the examined quinones exhibited instead a small brightness increase in the irradiated sheets, which could possibly be attributed to a photobleaching effect. Furthermore, Schmidt et al. (1995) found that methoxylated *ortho*-quinones, introduced into thermomechanical pulp by treatment with Fremy's salt, were bleached by 420 nm irradiation, whereas unmethoxylated *ortho*-quinones, generated by treatment with sodium periodate, were not.

Several researchers have reported that methylated and particularly acetylated lignocellulosic materials can be photobleached during irradiation (Callow 1947; Callow, Speakman 1949; Manchester et al. 1960; Andrews, Des Rosiers 1966; Lorås 1968; Ek et al. 1992; Paulsson et al. 1995). The photobleaching of acetylated materials has been ascribed to the formation of acetyl peroxide or peroxides formed from the carbohydrate acetates during irradiation (Callow, Speakman 1949; Lorås 1968). When comparing the degree of yellowing of acetylated high-yield pulps, aged under different light sources, with the degree of yellowing for untreated high-yield pulps, it is evident that the photostabilization obtained by the acetylation treatment not only is an effect of retarding the color-forming reactions, but also is a result of promoting photobleaching reactions. The results from aging experiments with the UV-fluorescent lamps give an assessment of the UV-light aging properties, i.e., a measurement of the chromophore-retarding effect of acetylation (cf. a in Figs. 3 to 6). The photobleaching response of acetylated pulps is illustrated for the sheets aged with the UV/VIS-fluorescent lamps (b in Figs. 3 to 6).

It is difficult to explain the photobleaching effect, obtained for acetylated mechanical pulps, in terms of coniferaldehyde or *ortho*-quinone photobleaching. The brightening effect of hydrogen peroxide has been attributed to a reaction with chromophoric carbonyl structures in the lignin. Several investigations have shown that hydrogen peroxide bleaching removes most (but not all) of the coniferaldehyde units in the lignin (Hirashima, Sumimoto 1987; Pan et al. 1992; Pan et al. 1994; Agarwal, McSweeny 1995; Agarwal et al. 1995; Schmidt, Heitner 1995). Quinone- and coniferaldehyde-type chromophores can also be eliminated by reaction with dithionite (cf. Dence, Reeve 1996). Furthermore, model compound studies have shown that acetylation rapidly decomposes most of the *ortho*-quinone units, whereas the *para*-quinones were essentially unaffected (Paulsson et al. 1996b). The significance of the remaining coniferaldehyde structures, *ortho*- and *para*-quinones, diguaiacylstilbenes (cf. Castellan et al. 1990; Gellerstedt, Zhang 1992; Gellerstedt, Zhang 1993; the term guaiacyl refers to a 4-hydroxy-3-methoxyphenyl residue), or some other still unknown structure for the photobleaching (and brightness stability) needs to be investigated further.

Optical properties of irradiated, acetylated and/or UV-screen impregnated aspen CTMP

A previous investigation has shown that efficient inhibition of photoyellowing was obtained when moderate amounts of UV-screens, such as 2-hydroxy-4-methoxybenzophenone (HMB) or Tinuvin 384 (a benzotriazole derivative), were applied onto acetylated sheets (Paulsson, Ragauskas 1997). Figure 7 shows the brightness change during irradiation of acetylated and/or HMB-treated sheets made of hydrogen-peroxide-bleached aspen CTMP. The effect of Tinuvin 384 was, in general, the same, and will therefore not be discussed further. As can be seen in the figure, the irradiation source chosen for reversion studies of additive-treated (or chemically modified) high-yield pulps has a crucial role in the outcome of the experiments and thereby the judgment of the effectiveness of a photostabilizing treatment. The HMB-treated sheets exhibited a good photostability when exposed to UV-radiation, probably due to a good match of the wavelength distribution of the light source (see Fig. 7a). When exposed to a broader wavelength range, the photostabilizing effect of the UV-absorbing compounds was different. Although UV/VIS-fluorescent lamps emit light in the ultraviolet range, the HMB-treated sheets showed no increased resistance toward photoaging when irradiated with this light source as compared to the control or acetylated sheets, respectively (Fig. 7b). The use of the xenon light source (Fig. 7c) gave aging results that were comparable with those obtained with the UV-lamps, although the photostabilizing effect of UV-screens were less and the effect of acetylation more pronounced than was the case when subjected to ultraviolet radiation alone.

Although the different light sources tested in this investigation gave a comparable degree of reversion for most of the untreated pulps, the effect of different irradiation techniques, i.e., spectral distribution of the light source used, considerably altered the photostabilizing effect of chemical modification (e.g., acetylation) and addition of UV-screens. The discrepancy in effectiveness of an inhibiting treatment reported in the literature can, in many cases, be explained in terms of the different exposure techniques used by the researcher/laboratory.

Sequential irradiation of untreated and acetylated, high-brightness aspen CTMP using UV- and UV/VIS-fluorescent lamps

The changes in TAPPI brightness, as a function of irradiation time under different irradiation sources, for the untreated and acetylated hydrogen-peroxide-bleached aspen CTMP are presented in Figures 8a and b. The changes in brightness for the handsheets irradiated with only one light source are given as a comparison in the figure (filled symbols). When comparing the sequence UV-fluorescent lamps – UV/VIS-fluorescent lamps, it is evident that irradiation with wavelengths of 300 to 420 nm generated colored structures that partly could be removed by irradiation with a more broader wavelength range (e.g., visible light). The photobleaching effects for the acetylated, UV-irradiated handsheets were much larger than for the irradiated control; a brightness gain of about 12 brightness units was obtained for the acetylated sheets compared with 7 units for the control (see Fig. 8a). Furthermore, the difference in brightness between the sequential irradiated (UV + UV/VIS) and the UV/VIS irradiated, acetylated CTMP was in the range of 3-4 brightness units after 400 hours of irradiation, i.e., only a small amount of the chromophores generated during UV-exposure of acetylated high-brightness aspen CTMP was not photobleachable. The corresponding value for the control was 7 brightness units. Figure 8b shows the photoyellowing effect of the irradiation sequence UV/VIS-fluorescent lamps – UV-fluorescent lamps. When the CTMP was acetylated to a high degree (acetyl content, 10.3%), the brightness, after the sequential irradiation procedure (400 + 4 h), was almost the same as after UV-exposure alone. There was, however, a

decrease in brightness for the low acetylated CTMP (acetyl content of 4.1%, ca. 8.5 brightness units) and for the control (ca. 16.3 units).

The photobleaching of a photoyellowed pulp has been reported by several researchers. Claesson et al. (1968) reported that high-yield bisulfite liner and newsprint made from mechanical pulp yellowed on irradiation with ultraviolet radiation of 365 nm, but that a bleaching of the yellow color was observed in visible light (436 nm). Forsskåhl and Tylli (1993) found that the maximum photobleaching of photoyellowed, unbleached, and bleached chemimechanical pulp occurred on irradiation at 420 to 430 nm; the brightening effect was, however, small compared to the discoloration observed. The results from the present investigation have shown that photobleaching of preyellowed (UV-irradiated, λ_{max} = 350 nm), untreated, and acetylated high-brightness aspen CTMP sheets occurs when the sheets are exposed to visible light (e.g., UV/VIS-fluorescent lamps, λ_{max} = 575 nm). It is also evident that acetylation (of the pulp) suppresses the color-forming reactions, while the photobleaching reactions are favored, both for nonirradiated and preyellowed handsheets.

Conclusions

The different irradiation sources used (e.g., ultraviolet "blacklight" fluorescent lamps, UV/VIS-fluorescent lamps, and a xenon burner) gave comparable aging results for the untreated spruce pulps, whereas the high-brightness aspen CTMP showed some variation in the degree of yellowing. The high-brightness aspen CTMP was, however, the most resistant pulp toward irradiation followed by the dithionite-bleached spruce TMP and the hydrogen-peroxide-bleached spruce CTMP. The hydrogen-peroxide-bleached spruce TMP was the most light-sensitive pulp to all of the light sources examined.

The loss in brightness for the acetylated pulps was strongly dependent on the light source used and was in the order: UV-fluorescent lamps>xenon lamp>>UV/VIS-fluorescent lamps. Photobleaching of the acetylated pulps was observed when exposed to radiation from the UV/VIS-fluorescent lamps. Furthermore, the UV-screen treated, high-brightness aspen CTMP showed a good photostabilization effect when exposed to radiation from the UV-fluorescent lamps or xenon lamp, but no retarding effect was observed under aging with the UV/VIS-fluorescent lamps, i.e., the irradiation source used for accelerated aging of chemically modified or additive-impregnated high-yield pulps has a decisive role in the judgment of a photostabilizing treatment.

The chromophores generated during irradiation of aspen CTMP with ultraviolet radiation was found to be partially decolored by exposure to light from the UV/VIS-fluorescent lamps (e.g., visible light, λ_{max} = 575 nm); an effect that was more pronounced for the acetylated pulps. Furthermore, the photostabilizing effect of acetylation is, most likely, a function of both retarding the reactions that generate colored chromophores and promoting photobleaching reactions. These results suggest that, although the acetylation methodology employed to generate UV/VIS-photostable lignin-containing paper not yet are suitable for commercial applications, the photostability of these handsheets is significant. Further studies are needed to determine the fundamental principles contributing to the photobleaching effect of acetylated high-yield pulps.

The present investigation has shown the necessity to develop a standard procedure for accelerated testing of the light-induced aging of lignin-containing materials.

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Figure captions

Fig. 1. Spectral characteristics of the tested irradiation sources. The spectral energy distributions of standard "cool white" fluorescent color (Waymouth 1992) and natural daylight (Merrigan 1975) are given in ***b*** *(broken line) and* ***c*** *(dotted line), respectively. Abbreviations: RPR 3500Å = UV-fluorescent lamps; RPR 5750Å = UV/VIS-fluorescent lamps; Xe = xenon lamp.*

Fig. 2. The change in TAPPI brightness after accelerated light-induced aging of different types of mechanical pulps. Abbreviations as in Fig. 1. Legends: (□), dithionite-bleached spruce TMP; (◊), hydrogen-peroxide-bleached spruce TMP; (○), hydrogen-peroxide-bleached spruce CTMP; (Δ), hydrogen-peroxide-bleached aspen CTMP.

Fig. 3. The change in TAPPI brightness after accelerated light-induced aging of untreated (□) and acetylated dithionite-bleached spruce TMP. Abbreviations as in Fig. 1. Legends (acetyl content): (◊), 6.2%; (○), 10.6%.

Fig. 4. The change in TAPPI brightness after accelerated light-induced aging of untreated (□) and acetylated hydrogen-peroxide-bleached spruce TMP. Abbreviations as in Fig. 1. Legends (acetyl content): (◊), 3.5%; (○), 6.7%.

Fig. 5. The change in TAPPI brightness after accelerated light-induced aging of untreated (□) and acetylated hydrogen-peroxide-bleached spruce CTMP. Abbreviations as in Fig. 1. Legends (acetyl content): (◊), 4.6%; (○), 9.4%.

Fig. 6. The change in TAPPI brightness after accelerated light-induced aging of untreated (□) and acetylated hydrogen-peroxide-bleached aspen CTMP. Abbreviations as in Fig. 1. Legends (acetyl content): (◊), 4.1%; (○), 6.0%; (Δ), 9.7%; (∇), 10.3%.

Fig. 7. The change in TAPPI brightness after accelerated light-induced aging of untreated (□) and 2-hydroxy-4-methoxybenzophenone-impregnated, acetylated hydrogen-peroxide-bleached aspen CTMP. Abbreviations as in Fig. 1. Legends (application level UV-screen): ***a****: (◊), 0.0%; (○), 1.5%; (Δ), 1.5% (acetyl content, 6.0%).* ***b****: (◊), 0.0%; (○), 1.4%; (Δ), 1.2% (acetyl content, 6.0%).* ***c****: (◊), 0.0%; (○), 2.0%; (Δ), 1.7% (acetyl content, 6.0%).*

Fig. 8. The change in TAPPI brightness after sequential irradiation (UV-fluorescent lamps and UV/VIS-fluorescent lamps) of hydrogen-peroxide-bleached aspen CTMP. Filled symbols indicate that the handsheets have been irradiated with only one of the light sources. Abbreviations as in Fig. 1. Legends (acetyl content): (□), untreated; (◊), 4.1%; (○), 10.3%.

Table 1. Change in optical properties on acetylation of different high-yield pulps. Acetylation times (min) are given within parentheses.

Pulp		Acetyl content, % by mass	TAPPI brightness, %	L*	a*	b*	PC_1-number[a]
TMP (spruce), dithionite-bleached							
Control		1.4	65.7	92.1	-0.4	13.6	0.00
Acetylated	(5)[b]	6.2	66.5	92.4	-0.5	13.2	-0.52
	(15)[b]	10.6	67.5	92.8	-0.6	13.0	-1.13
TMP (spruce), H_2O_2-bleached							
Control		0.2	75.0	95.0	-1.7	10.7	0.00
Acetylated	(5)[b]	3.5	73.7	94.9	-1.8	11.6	0.53
	(15)[b]	6.7	72.7	94.9	-1.9	12.4	0.93
CTMP (spruce), H_2O_2-bleached							
Control		0.5	78.2	95.4	-1.9	8.8	0.00
Acetylated	(5)[b]	4.6	76.3	95.2	-2.0	10.0	0.64
	(15)[b]	9.4	75.6	95.1	-2.1	10.4	0.90
CTMP (aspen), H_2O_2-bleached							
Control		0.6	84.3	95.8	-1.0	4.3	0.00
Acetylated	(5)[b]	4.1	80.9	95.3	-1.4	6.4	0.87
	(10)[b]	6.0	78.5	94.9	-1.3	7.6	1.56
	(10)[c]	9.7	74.3	93.7	-1.1	8.8	3.06
	(25)[b]	10.3	73.7	93.7	-1.1	9.3	3.31

[a]The post-color (PC_1) number at 457 nm (due to acetylation) was calculated according to Giertz (1945), Eqs. [1] and [2].

[b]Acetylation temperature, 100 ° C.

[c]Acetylation temperature, 110 ° C.

Table 2. Change in optical properties on light-induced aging of untreated and acetylated high-yield pulps. Acetylation times (min) are given within parentheses.

Pulp		Acetyl content, % by mass	TAPPI brightness, %	UV-fluorescent tubes Irradiation time: 4 h			UV/VIS-fluorescent tubes Irradiation time: 216 h			Xenon lamp Irradiation time: 40 h		
				TAPPI brightness, %	PC_2-number[a]	Δk[b]	TAPPI brightness, %	PC_2-number[a]	Δk[b]	Brightness[c], %	PC_2-number[a]	Δk[b]
TMP (spruce), dithionite-bleached												
Control		1.4	65.7	45.6	23.4	10.3	45.6	23.3	10.3	44.9	24.6	10.9
Acetylated	(5)[d]	6.2	66.5	50.9	15.3		60.7	4.3		54.1	11.3	
	(15)[d]	10.6	67.5	56.2	9.3		68.3	-0.5		60.1	5.5	
TMP (spruce), H_2O_2-bleached												
Control		0.2	75.0	49.7	21.3	11.2	47.3	25.2	13.3	48.4	23.5	12.4
Acetylated	(5)[d]	3.5	73.7	53.9	15.1		64.8	4.9		56.2	12.6	
	(15)[d]	6.7	72.7	58.5	9.6		73.9	-0.5		64.3	4.9	
CTMP (spruce), H_2O_2-bleached												
Control		0.5	78.2	49.6	22.5	10.9	48.2	24.8	12.0	48.4	24.4	11.8
Acetylated	(5)[d]	4.6	76.3	53.0	17.2		63.9	6.5		55.5	14.4	
	(15)[d]	9.4	75.6	59.0	10.3		73.5	0.8		61.5	8.4	
CTMP (aspen), H_2O_2-bleached												
Control		0.6	84.3	55.6	16.2	6.2	66.5	7.0	2.7	58.2	13.4	5.1
Acetylated	(5)[d]	4.1	81.0	59.0	12.0		77.0	1.3		64.0	8.2	
	(10)[d]	6.0	78.6	61.2	9.3		80.0	-0.4		67.7	5.1	
	(10)[e]	9.7	74.6	63.8	6.1		81.5	-2.1		70.7	2.3	
	(25)[d]	10.3	73.7	64.5	5.0		82.1	-2.5		70.8	1.9	

[a]The post-color (PC_2) number at 457 nm (due to irradiation) was calculated according to Giertz (1945), Eqs. [1] and [2].

[b]The change in light absorption (Δk) was calculated from the PC_2-value with the assumption of constant light scattering according to Johnson (1989), Eq. [3].

[c]Brightness measured with an Elrepho 2000 spectrophotometer. This instrument uses a diffuse light source and measures the reflected light at a 0° viewing angle, i.e., the "Elrepho" brightness cannot directly be translated to TAPPI brightness that is determined with an instrument employing a directional light source (incident angel of 45°) and measures the reflected light at a 0° viewing angle. The difference in measured brightness was, however, small between the two instruments (approximately 1 brightness unit).

[d]Acetylation temperature, 100° C.

[e]Acetylation temperature, 110° C.

Figure 1

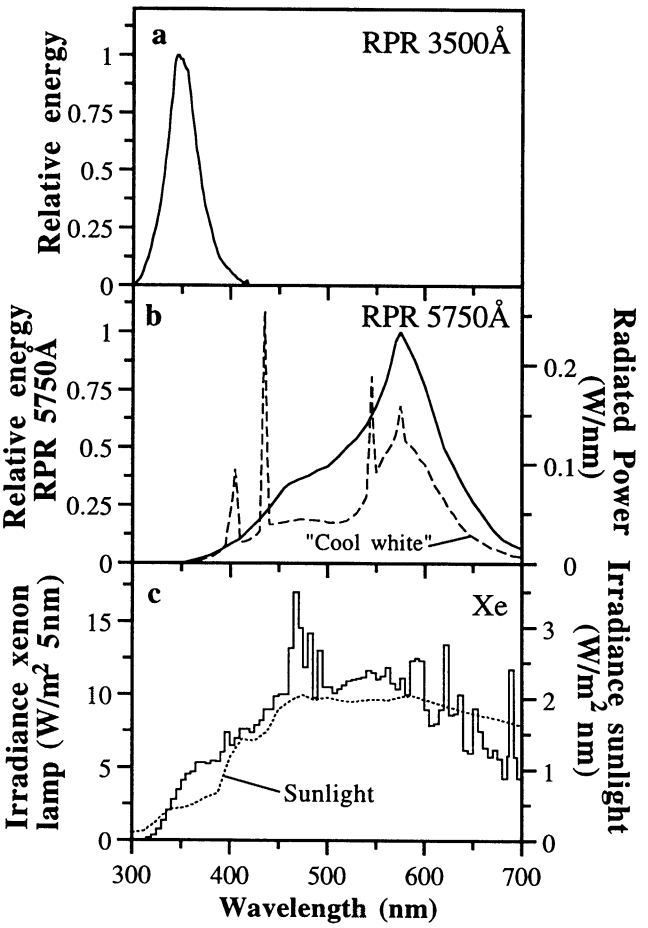

a
RPR 3500Å
Relative energy
b
RPR 5750Å
Relative energy RPR 5750Å
Radiated Power (W/nm)
"Cool white"
c
Xe
Irradiance xenon lamp (W/m² 5nm)
Irradiance sunlight (W/m² nm)
Sunlight
Wavelength (nm)

Figure 2

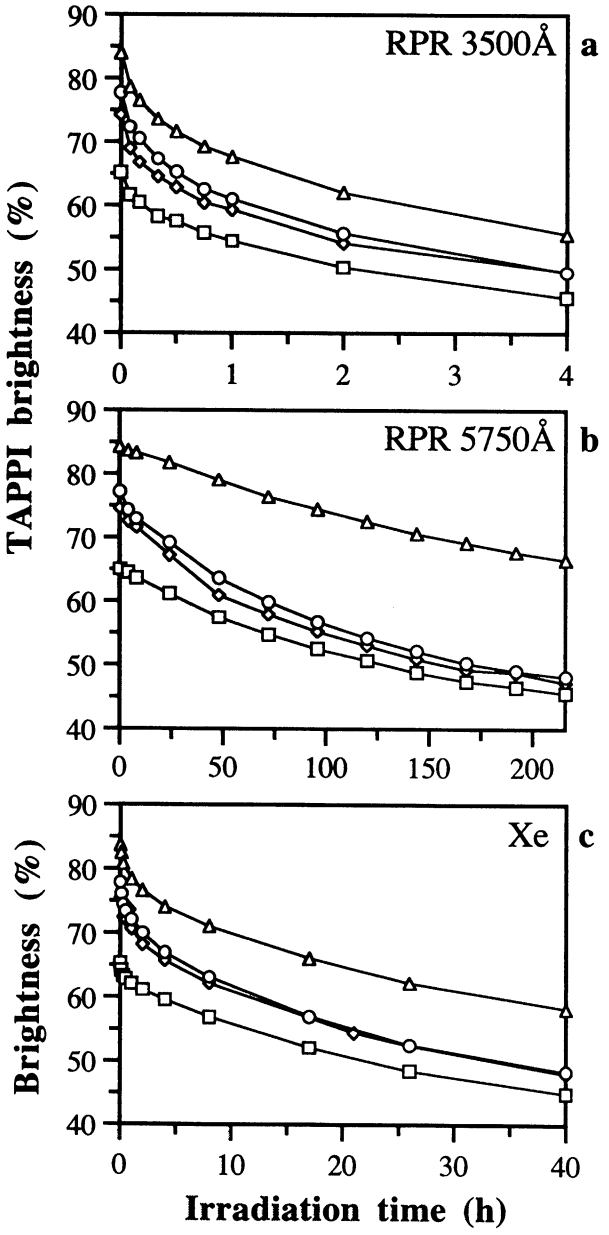

RPR 3500Å
a
RPR 5750Å
b
Xe
c
TAPPI brightness (%)
Brightness (%)
Irradiation time (h)
90
80
70
60
50
40
0
1
2
3
4
50
100
150
200
10
20
30
40

Figure 3

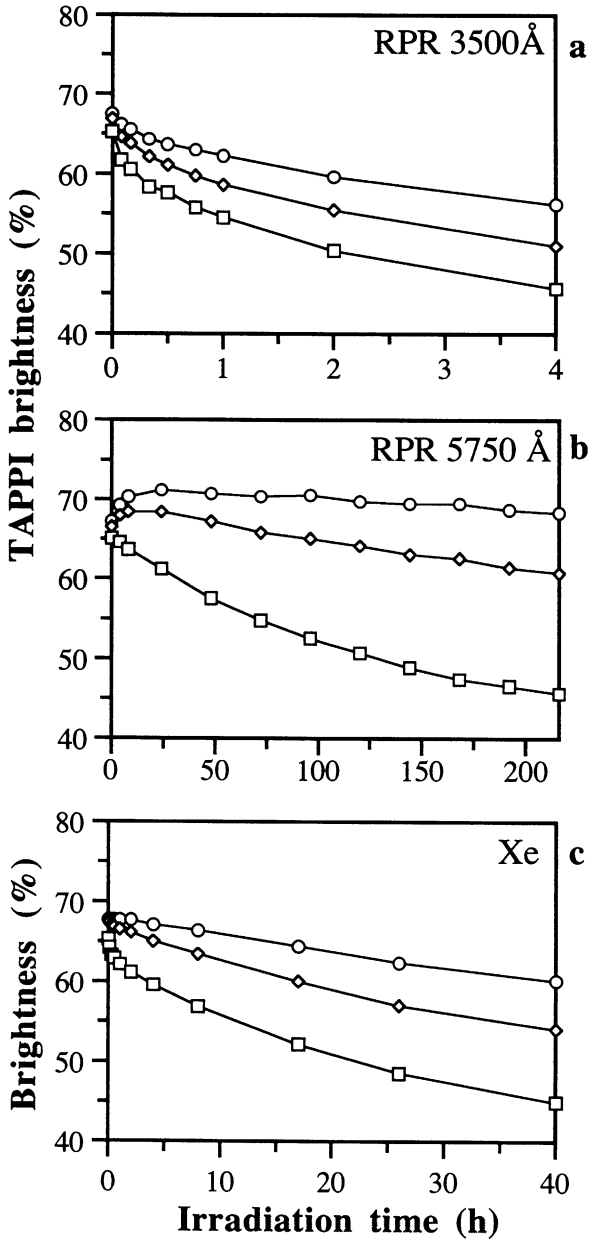

RPR 3500Å
a
RPR 5750 Å
b
Xe
c
TAPPI brightness (%)
Brightness (%)
Irradiation time (h)
80
70
60
50
40
0
1
2
3
4
50
100
150
200
10
20
30

Figure 4

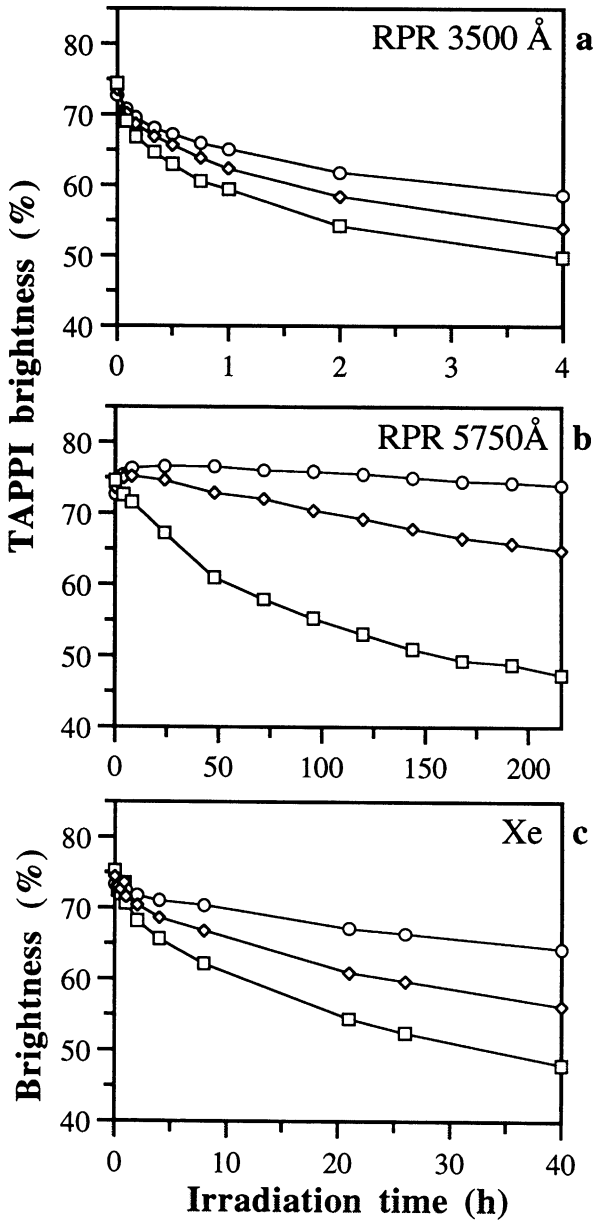

RPR 3500 Å
a
RPR 5750Å
b
Xe
c
TAPPI brightness (%)
Brightness (%)
Irradiation time (h)
80
70
60
50
40
0
1
2
3
4
50
100
150
200
10
20
30

Figure 5

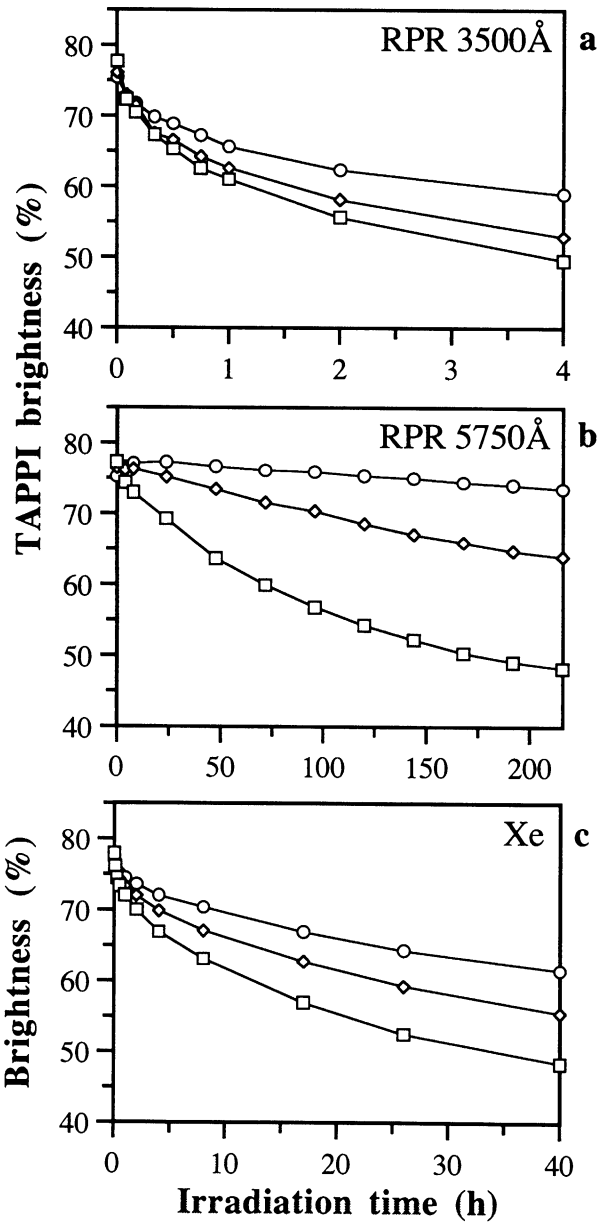

RPR 3500Å
a
RPR 5750Å
b
Xe
c
TAPPI brightness (%)
Brightness (%)
Irradiation time (h)
80
70
60
50
40
0
1
2
3
4
50
100
150
200
10
20
30

Figure 6

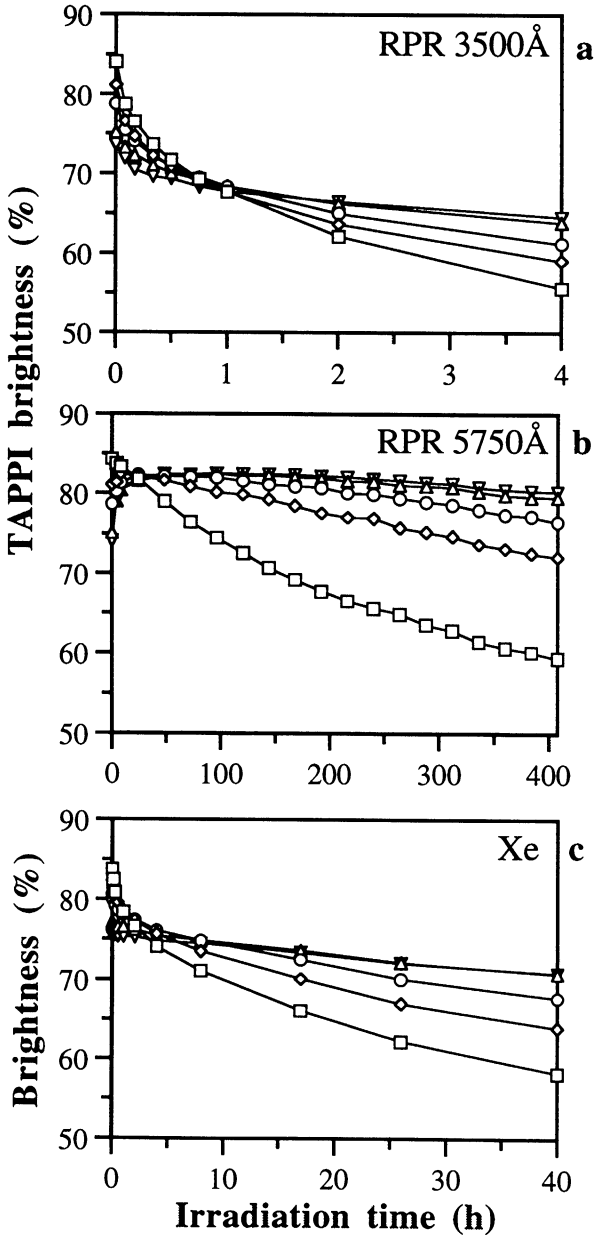

RPR 3500Å
a
RPR 5750Å
b
Xe
c
TAPPI brightness (%)
Brightness (%)
Irradiation time (h)
90
80
70
60
50
0
1
2
3
4
100
200
300
400
10
20
30
40

Figure 7

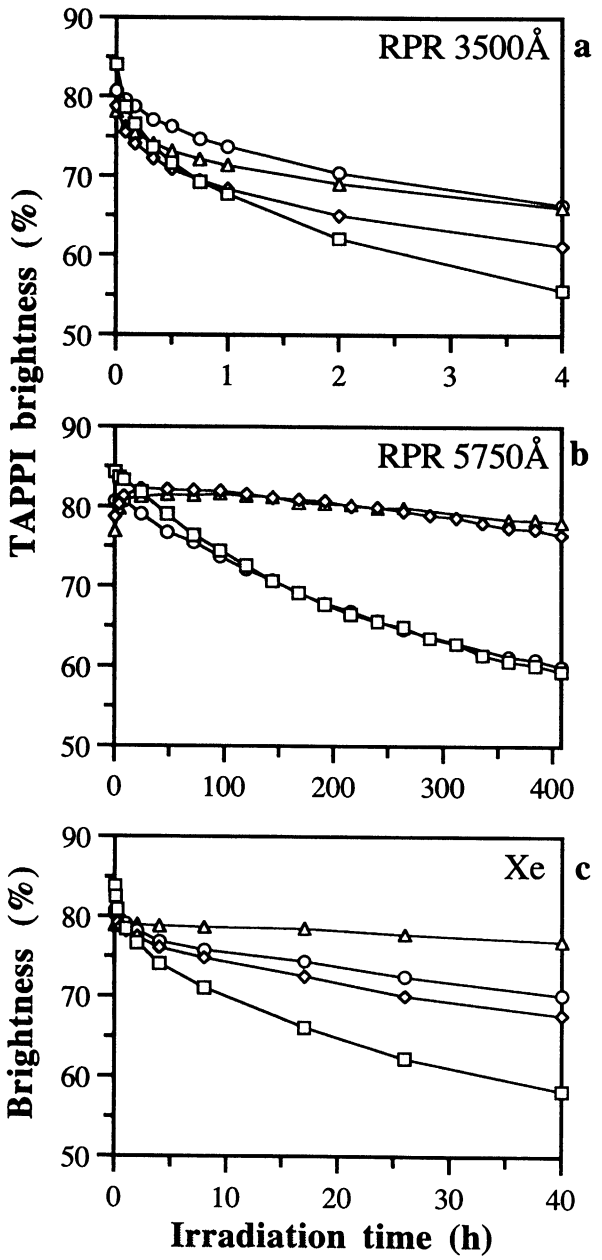
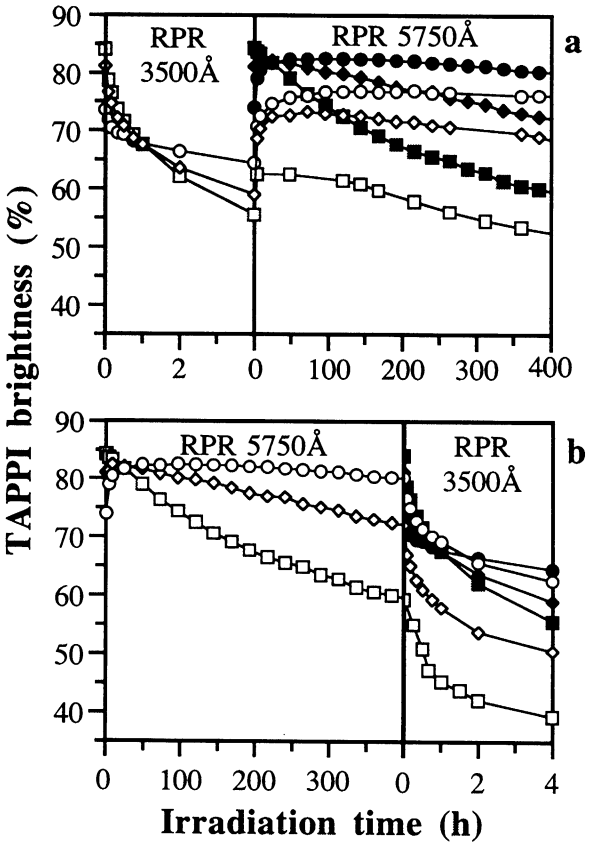

RPR 3500Å
a
RPR 5750Å
b
Xe
c
TAPPI brightness (%)
Brightness (%)
Irradiation time (h)
90
80
70
60
50
0
1
2
3
4
100
200
300
400
10
20
30
40

Figure 8


RPR
3500Å
RPR 5750Å
a
RPR 5750Å
RPR
3500Å
b
TAPPI brightness (%)
Irradiation time (h)
90
80
70
60
50
40
0
2
100
200
300
400
4

Chemical modification of lignin-rich paper

Part 10. The light-induced yellowing of untreated and acetylated high-yield pulps studied by solid-state UV/VIS diffuse reflectance spectroscopy

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Keywords: Acetylation, Absorption difference spectra, Thick handsheets, Irradiation, Light source, Chemithermomechanical pulp, Yellowing, Inhibition, Hydrogen-peroxide-bleached

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SUMMARY: Untreated and acetylated hydrogen-peroxide-bleached aspen CTMP and hydrogen-peroxide-bleached spruce CTMP were subjected to accelerated light-induced aging using three different types of light-sources (UV-fluorescent lamps, λ_{max}=350 nm and UV/VIS-fluorescent lamps λ_{max}=425 and 575 nm). The photochemical changes that took place during acetylation and irradiation were followed by solid-state UV/VIS diffuse reflectance spectroscopy.

The wavelength distribution of the irradiation source strongly influenced the photochemistry of both untreated and acetylated pulps. Absorption difference spectra of aspen CTMP, irradiated with the UV-lamps, exhibited an apparent absorption maxima at 370 nm with a shoulder at 415 nm, whereas the UV/VIS-fluorescent lamps irradiated aspen CTMP exhibited an absorption peak at 360 nm and substantially less absorption in the entire visible region (λ>400 nm). Two major absorption peaks, at 330-345 nm and at 425 nm, were observed in the UV/VIS absorption difference spectra of irradiated spruce CTMP regardless of the irradiation source used. However, in addition to the photodiscoloration, a photobleaching with λ_{max}~390 nm was observed when the spruce CTMP was irradiated with the two types of UV/VIS-fluorescent lamps. Acetylation was found to slow down the UV-light induced reactions, but could also promote photobleaching reactions when subjected to an irradiation source emitting light in the visible range. Generally, no further discoloration was observed when the acetylated CTMPs (acetyl content, 8-10%) were irradiated with the UV/VIS-fluorescent lamps under the aging conditions used in this work.

This investigation has shown the importance of choosing a light source that resembles the actual reversion situation as close as possible (e.g., contain both an ultraviolet and a visible component) if realistic accelerated light-induced reversion conditions are to be obtained.

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During the last decade, pulping processes have been developed that can produce high-performance, lignin-containing pulps (e.g., hydrogen-peroxide-bleached chemithermomechanical pulps, CTMP) at significantly lower capital and operating costs than kraft pulps. Mechanical pulps use the forest resources more efficiently, and because of the use of nonchlorine-based bleaching chemicals, full mill closure is currently possible (Stevenson 1992). Further, the simple process technology allows for economical construction of new pulping capacity in small units (ca. 250 tons/day). Hardwood high-yield pulps can be bleached to a brightness level of 86-88% ISO, i.e., sufficiently high for most high-quality communication papers. Furthermore, at a substitution degree of 25% in the sheet, high-yield hardwood pulps can offer the papermaker a substantial economical savings in the range of $10-40/ton of paper (Ford, Sharman 1996).

In spite of the many positive features these new generation of high-yield pulps possess, mechanical pulps are mainly used for the production of short-lived, low-value paper grades. This is because a lengthy exposure to daylight (i.e., ultraviolet light) causes a discoloration (yellowing) that is unacceptable in many applications. It is mainly light-induced reactions in the lignin part of the pulp constituents that causes the discoloration (cf. Heitner, Schmidt 1991; Leary 1994).

There still are uncertainties about the reactions leading to colored structures during photoyellowing or what the final chemical structures of the colored products are. It was early suggested that quinones, quinone methides, and cyclohexadienones generated from phenoxyl radicals are the initially formed colored products (Leary 1968a; Leary 1968b; Lin, Kringstad 1971). Irradiation of lignin model compounds in the presence of oxygen showed that different types of reactions could occur in the photooxidation process (Lin, Kringstad 1971). First, a demethylation reaction that generates *ortho*-quinonoid structures. This is in accordance with the loss of methoxyl groups observed for irradiated groundwood (Forman 1940; Lewis, Fronmuller 1945; Leary 1968a). It is also possible that *para*-quinonoid structures, formed through side-chain displacement, could contribute to color formation although to a lesser extent than *ortho*-quinonoid structures (Lin, Kringstad 1971). Other investigations have, however, stated that side-chain elimination to produce primarily hydroquinones (*para*-quinones) is the main reaction pathway during photoyellowing (Gellerstedt, Pettersson 1977, cf. Forsskåhl et al. 1991; Hirashima, Sumimoto 1994; Agarwal 1997). A third possibility is 5-5 coupling of phenoxyl radicals to form colored biphenyl compounds (cf. Forsskåhl 1994).

Exposure of CTMP and TMP (thermomechanical pulp) to ultraviolet radiation with a wavelength of 300-400 nm produced chromophores with absorption maxima at 350 and 420 nm (Heitner, Min 1987). These chromophores were considered to be a methoxy-*p*-benzoquinone and an *ortho*-quinone with an aliphatic substituent in the 2-position. *Ortho*-quinonoidic structures have been detected in different types of high-yield pulps, both before and after irradiation. Lebo et al. (1990) found that about 75% of the increase in color during irradiation of white spruce refiner mechanical pulp was caused by the formation of *ortho*-quinones. Zhu et al. (1995) used fluorescence spectroscopy to confirm the presence of photochemically generated *ortho*-quinones in several hydrogen-peroxide-bleached high-yield pulps. Schmidt et al. (1995) reported that both methoxylated and unmethoxylathed *ortho*-quinones were likely to be introduced in peroxide-bleached mechanical pulps during irradiation. Monomeric *ortho*-quinones were suggested to be the major chromophores formed during light-induced yellowing of lignin-rich pulps based on UV/VIS reflectance spectroscopy of peroxide-bleached GWP (groundwood pulp), CTMP, and quinonoid lignin model compounds (Zhang, Gellerstedt 1994a). Stilbene *ortho*-quinones were reported to be the only colored products formed when monohydroxystilbenes (deposited on the

surface of a filter paper) were exposed to UV radiation (Zhang, Gellerstedt 1994b). Furthermore, the chromophores produced by UV radiation were found to be almost completely removed by sodium borohydride reduction (Hemmingson, Morgan 1990; Capretti et al. 1994; Schmidt, Heitner 1995; Pan, Ragauskas 1997). This suggests that most of the colored substances formed contain carbonyl structures (quinones, conjugated ketones, aldehydes) that can be reduced by $NaBH_4$.

Argyropoulos et al. (1995) used solid-state ^{31}P NMR spectroscopy on samples of irradiated unbleached and hydrogen-peroxide-bleached GWP (oxyphosphorylated) in order to determine the early photochemical changes that occur during light-induced yellowing. The data suggested that *ortho*-quinones initially produced during irradiation subsequently reacted to form more complex carbonyl chromophoric structures which do not have a quinonoid character. It was also found that *ortho*-quinones were converted faster in the unbleached pulp than in the peroxide-bleached pulp. The bleached pulp contains more stilbenes that could be converted to stilbene *ortho*-quinones during irradiation (Zhang, Gellerstedt 1994b), and it is possible that these structures require longer irradiation times to be eliminated. The conversion of quinones to more complex chromophores could explain why no quinones or quinonoid structures were detected in irradiated milled wood lignin (Sjöholm et al. 1992).

Forsskåhl and Janson (1991a) reported that the two main chromophores (displaying bands at 370 and 430 nm), generated by irradiation of chemimechanical pulps, were interrelated. Irradiation at a short wavelength (373 nm) creates a colored chromophore, while irradiation at the longer wavelength (435 nm) leads to the formation of a colorless product. These authors suggest that there are several possible candidates for such a system; a hydroquinone-quinone system, charge transfer complexes, possibly quinone methides and also cis-trans isomerism of aromatic conjugated double bonds. The same effect was later found for irradiated unbleached and peroxide-bleached thermomechanical pulps (Forsskåhl, Maunier 1993). Schmidt et al. (1995) reported that methoxylated *ortho*-quinones could be bleached by 420 nm irradiation, whereas unmethoxylated *ortho*-quinones sensitized destruction of aromatic groups. Robert and Daneault (1995) observed two major absorption peaks at 360 and 425 nm when TMP paper (black spruce/balsam fire mixture) was exposed to UV light (λ, 300-400 nm). The peak at 360 nm was the result of the disappearance of one chromophore and the appearance of a different chromophore. The other peak (425 nm) was the result of the formation of three chromophores.

It is important to bear in mind that quinonoidic structures are themselves photosensitizers and that they can thus contribute to further chromophore formation (Gierer, Lin 1972; Neumann, Machado 1989; Ek 1992; Forsskåhl et al. 1993; Castellan et al. 1993).

The present communication describes the effect of acetylation on the light-induced yellowing of hydrogen-peroxide-bleached aspen CTMP and hydrogen-peroxide-bleached spruce CTMP, the pulps most often suggested as replacement for chemical pulps in high-quality paper grades. The mechanism of stabilization (and yellowing) has been studied using solid-state UV/VIS diffuse reflectance spectroscopy performed on high basis weight (200 $g \cdot m^{-2}$) handsheets. The effect of three irradiation sources with different wavelength distributions on the light-induced yellowing will also be discussed.

Experimental

Pulps and paper samples. Commercially produced hydrogen-peroxide-bleached spruce (*Picea abies*) and aspen (*Populus tremuloides*) CTMP were used as received for the studies described in this paper. The pulps were obtained as dried samples. The high-brightness hardwood CTMP was manufactured employing hydrogen peroxide both as a chemical pretreatment and as a bleaching stage. Handsheets (200 $g \cdot m^{-2}$) were prepared according to TAPPI Test Method T 205 om-88. The paper sheets were then conditioned at 23°C and 50% r.h. according to TAPPI Test Method T 402 om-88 before further treatment.

Acetylation procedure. The handsheets [cut into strips (30 x 75 mm)] were acetylated (at 100°C) according to the procedure described by Paulsson et al. (1994).

Analyses. The acetyl content was calculated from the amount of acetate liberated after saponification with sodium hydroxide as previously described in Paulsson et al. (1996a). The acetyl content is given as a percentage of the dry weight of the paper.

UV/VIS diffuse reflectance spectroscopy. UV/VIS spectra were recorded on a Perkin Elmer Lambda 19 DM spectrophotometer equipped with a diffuse reflectance and transmittance accessory (Labsphere RSA-PE-90). The accessory is essentially an optical bench which includes double beam transfer optics and a six-inch diameter (154 mm) integrating sphere. Background correction was made with a SRS-99-010-7890 standard. The absorbance (*ABS*) was calculated from the diffuse reflectance (R_∞) using the following expression derived from the Beer-Lambert law (cf. Robert, Daneault 1995): $ABS = -\log R_\infty$. The resulting spectra were averaged from four to six measurements.

Accelerated light-induced yellowing. The paper samples were subjected to an accelerated photoyellowing in a Rayonet photochemical reactor (Model RPR 100, The Southern New England Ultraviolet Company, Branford, CT, USA) equipped with eight RPR 3500Å UV-fluorescent ("blacklight") lamps, eight RPR 4190Å UV/VIS-fluorescent lamps, or eight RPR 5750Å UV/VIS-fluorescent lamps and a merry-go-round apparatus for uniform irradiation. All lamps were obtained from The Southern New England Ultraviolet Company. The temperature was kept close to room temperature by a cooling fan (to minimize heating of the sample). The temperatures were 29°C, 31°C, and 27°C for the RPR 3500Å, RPR 4190Å, and RPR 5750Å lamps aged sheets, respectively. Figure 1 summarizes the spectral distribution of the three light sources, as received from the manufacturer. The spectral distribution of standard "cool white" fluorescent color used in many commercial lighting installations (Waymouth 1992, dotted line in Fig. 1) and natural daylight (Merrigan 1975, broken line) is given as a comparison. Untreated paper sheets were used in all radiation experiments as controls.

Optical measurements. TAPPI brightness and color changes according to the CIELAB color scale (L^*-, a^*-, b^*-values) were measured using a Technidyne Brightimeter (Model S-5) according to TAPPI Test Method T 452 om-92 and TAPPI Test Method T 524 om-94, respectively.

Results and discussion

Figure 1 shows the relative energy distribution of the three irradiation sources used for accelerated aging in this work. The RPR 3500Å UV-lamps emit light in a band between 300 and 420 nm with an approximately Gaussian spectral distribution (λ_{max}=350 nm). The lamps lack,

however, the visible component of diffuse sunlight or office light. The RPR 4190Å UV/VIS-lamps have a slightly narrower emission band with a maximum at approximately 425 nm. The third irradiation source, RPR 5750Å, emits light in both the ultraviolet and visible range (from about 350 to 700 nm, λ_{max}= 575nm) and has a comparatively close match to the conventional standard "cool white" fluorescent color used in many commercial lighting installations (see dotted line in Fig. 1).

Absorption difference spectra of untreated, irradiated pulps

The interpretation of a UV/VIS absorption spectra at short wavelengths (e.g., below 340 nm) is difficult since the signal to noise ratio is low in this region (Robert, Daneault 1995). This is because the paper sample absorbs most of the light due to its thickness and its high lignin concentration. A complement to this study, in the low wavelength range, could be performed using low basis weight sheets (10 $g \cdot m^{-2}$) according to the procedure described by Schmidt and Heitner (1993a). Care should also be taken when evaluating the results after high UV exposures since the assumption of exponential distribution of chromophores in the thickness of the sheet may no longer be valid (cf. Robert, Daneault 1995). Nevertheless, solid-state UV/VIS diffuse reflectance spectroscopy, performed on thick handsheets and with the consideration of the above limitations, is a powerful technique for the study of light-induced yellowing of lignin-containing materials. The result that is obtained with this method is what the eye will perceive as "yellowing of a thick paper."

Figures 2a-c show the UV/VIS absorption difference spectra (ΔABS vs. wavelength) of hydrogen-peroxide-bleached aspen CTMP recorded after aging with various light sources. The change in optical properties on acetylation and irradiation is given in Table 1. It is evident that the choice of irradiation source strongly influenced the photochemistry. Although all of the light sources generated a discoloration in the entire visible region (λ>400 nm), the shape of the absorption curves was different. Irradiation with the RPR 3500Å UV-lamps generated an apparent absorption maxima at 370 nm with a shoulder at approximately 415 nm (Fig. 2a), whereas the RPR 4190Å and RPR 5759Å UV/VIS-lamps generated an absorption maxima at 360 nm and showed substantially less absorption in the λ>400 nm range (Figs. 2b-c). The spruce CTMP behaved somewhat differently as can be seen in Figs. 3a-c. Irradiation with the RPR 3500Å UV-lamps generated an apparent maxima at 330 nm and a distinct maxima at 425 nm. The RPR 4190Å and RPR 5759Å UV/VIS-lamps introduced two maxima; one at 330 nm that was shifted toward longer wavelengths (345 nm) after extensive reversion and one maxima at 425 nm. In addition to the photodiscoloration, a photobleaching with λ_{max}~390 nm was observed for the last two light sources (Figs. 3b-c).

Several research groups have used UV/VIS diffuse reflectance spectroscopy to study the yellowing phenomena. Schmidt and Heitner (1995) reported that hydrogen-peroxide-bleached aspen CTMP showed a single maximum at about 360 nm when exposed to broad-band UV radiation, but no shoulder at ~415 nm was detected. The high-brightness aspen CTMP used in the present investigation was pretreated with hydrogen peroxide, and it is possible that this treatment changes the chromophoric precursors in such a way that new colored substances, absorbing in the 415 nm region, were formed when subjected to UV-exposure. Generally, UV/VIS diffuse reflectance spectroscopy of hydrogen-peroxide-bleached softwood pulps (GWP, TMP, and CTMP) performed on both thin and thick sheets, shows an increased absorption in the

UV region at 320-360 mm and in the visible region at 410-435 nm when exposed to UV-radiation (Hirashima, Sumimoto 1986; Heitner, Min 1987; Fornier de Violet et al. 1989; Forsskåhl, Janson 1991b; Francis et al. 1991; Schmidt, Heitner 1991; Schmidt, Heitner 1993a,b; Zhang, Gellerstedt 1994a; Robert, Daneault 1995; Schmidt, Heitner 1995; Schmidt, Heitner 1997). The increase in absorption in the UV-region has been attributed to the formation of aromatic carbonyl groups (λ_{max}~330 nm) and to the formation of quinones [possibly methoxylated *para-* or *ortho*-quinones (monohydrate adduct see Schmidt, Heitner 1995, cf. Adler, Lundquist 1961), λ_{max}~350-370 nm]. It is also possible that coniferaldehyde with an absorption maximum at ~350 nm, generated through photooxidation of coniferyl alcohol, contributes to the UV-absorption peak. The increase in the absorption in the visible region is attributed to the formation of *ortho*-quinonoidic chromophores, at least in an initial phase.

The present investigation showed that regardless of the wavelength distribution of the irradiation source, absorption peaks appeared in the above-mentioned UV and visible regions during aging of hydrogen-peroxide-bleached spruce CTMP. The relationship between the peak areas and the position of the maxima was, however, dependent of the light source used. The photobleaching observed at short irradiation times for the two UV/VIS-lamps was somewhat more pronounced for the RPR 4190Å lamps. This was expected since these lamps emit light in the region where photobleaching is noticeable (Andrady et al. 1991; Forsskåhl, Janson 1991a). The decrease in absorption at 360 nm observed during irradiation of lignin-containing materials has been attributed to the destruction of coniferaldehyde end groups or to the conversion of quinones to colorless structures (Wang et al. 1995, cf. Castellan et al. 1993; Ragauskas 1993). The reduction in chromophore content at 390 nm cannot entirely be explained by the elimination of these structures since sulfonation and hydrogen peroxide bleaching eliminates most of the coniferaldehyde and quinonoidic structures (cf. Dence 1996). Hydroxystilbenes, that can be introduced in the lignin moiety during high-yield pulping and alkaline bleaching conditions (Gellerstedt, Agnemo 1980; Wu et al. 1991; Gellerstedt, Zhang 1992), have been proposed as the leucochromophore that, to a large extent, are responsible for the initial discoloration of bleached high-yield pulps (Gellerstedt, Zhang 1993, cf. Castellan et al. 1990). Simple stilbenes have an absorption maximum at about 330 nm in solution, but it is possible that this maxima can be shifted to higher wavelengths when incorporated in the lignin macromolecule due to steric and electronic effects of substituent groups. Zhang and Gellerstedt (1994a) reported a red-shift of the UV/VIS absorption maxima of quinone and stilbene model compounds in the solid state (on filter paper or on bleached GWP or CTMP) compared with the absorption in solution. The red-shift was 26 nm for a hydroxystilbene model and between 32 and 148 nm for quinonoidic compounds, an effect charge transfer complexes (quinone-phenol) might account for (Zhang, Gellerstedt 1994a; cf. Furman, Lonsky 1986; Furman, Lonsky 1988).

It is evident that measurements of brightness and L^*-, a^*-, and b^*-values hardly can give a complete and accurate description of a complicated photochemical process such as the discoloration of lignin-containing materials. For example, the brightness level of the irradiated spruce CTMP handsheets was approximately the same (46.7-48.5%, see Table 1) for the three light sources when compared at different reversion times. However, the photochemistry was not the same as can be seen in Fig. 4. Furthermore, it is also questionable to use a light source that only emits light in the ultraviolet range for reversion studies since the photochemistry in the presence of visible light is quite different and it may lead to the wrong conclusion regarding the reaction mechanism(s) and degree of yellowing (stabilization) (cf. Paulsson, Ragauskas 1998a).

[However, the UV-lamps give an assessment of the UV light-aging properties and could be useful when complications from other wavelengths are not desirable.]

Absorption difference spectra of acetylated pulps

It is known that the acetylation process influences brightness differently depending on the type of mechanical pulp derivatized (unbleached-bleached, softwood-hardwood, see Manchester et al. 1960; Paulsson et al. 1996a; Paulsson, Ragauskas 1998a). Figure 5 shows the UV/VIS absorption spectra (acetylated - unacetylated) for the two tested pulps. During acetylation of aspen CTMP, a substantial increase in the absorption is seen in the entire wavelength range 350-700 nm with maxima at approximately 370 and 430 nm. This corresponds to a decrease in brightness with 8 and 11 brightness units for a reaction time of 5 and 20 minutes, respectively (Table 1). The large loss in brightness for the hydrogen-peroxide-pretreated aspen pulp is contradictory to earlier reported results for hydrogen-peroxide-bleached high-yield pulps (cf. discussion in Paulsson, Ragauskas 1998b). Acetylation of the spruce CTMP induced a discoloration, indicated by the absorption increase at λ>410 nm, but also a bleaching at wavelengths below 410 nm (maximum at approximately 385 nm). Acetylation of model compounds, representative of chromophoric and leucochromophoric structures in lignin, has shown that catechols, hydroquinones, stilbenes, and coniferyl alcohol units were rapidly derivatized on acetylation (Paulsson et al. 1996b). Models of the *ortho*-quinonoid type, both methoxylated and unmethoxylated, were also rapidly decomposed and, to a large extent, decolored on acetylation, whereas structures of the *para*-quinonoid type were essentially unaffected. Further, a coniferaldehyde model was slowly derivatized yielding a derivative of the acylal type. Based on the above findings, the decrease at 385 nm could possibly be explained by the removal of a hydroxystilbene structure (cf. the discussion above dealing with a red-shift of the absorption maxima of stilbenes in the solid state). The peaks at 370 and 430 nm could result from the characteristic UV absorption of methoxylated *para*-quinones and visible absorption of *ortho*-quinones, respectively. The absorption peak at 455 nm is close to the absorption peak of a stilbene *ortho*-quinone structure incorporated on bleached CTMP (λ_{max}=460 nm, see Zhang, Gellerstedt 1994a).

Absorption difference spectra of acetylated, irradiated pulps

Figures 6a-c and 7a-c show the effect of different irradiation times and different irradiation sources on the UV/VIS absorption difference spectra of acetylated aspen CTMP and acetylated spruce CTMP, respectively. In these figures, the solid lines represent the test sheets acetylated for 20 minutes. The photoaging properties for the low acetylated sheets (5 minutes) were, in general, the same, although shifted to a somewhat lower stability level as indicated by the lower acetyl content and will therefore not be discussed further. However, UV/VIS spectra for the low acetylated test sheets irradiated for the longest time (24, 349, and 312 hours depending on light source) are given as a comparison in Figs. 6 and 7.

It was interesting to see if acetylation, an efficient way to retard yellowing of different types of high-yield pulps, fundamentally changed the photochemistry or only slowed down the rate of chromophore formation, as judged from the UV/VIS absorption spectra. The acetylated aspen CTMP, irradiated with the RPR 3500Å UV-lamps, generated an apparent absorption maxima in the same region as the unacetylated CTMP (λ, 370 nm, Fig. 6a). No shoulder at 415 nm was, however, observed, and the increase in absorption was less in the whole UV-visible region (cf.

Fig. 2a). The two light sources that emitted light in both the ultraviolet and visible ranges induced a photobleaching in the visible range. The absorption in the UV-part of the spectra was also less and shifted about 20 nm toward lower wavelengths (cf. Figs. 2b-c and Figs. 6b-c). The photobleaching resulted in a substantial brightness increase as can be seen in Table 1; the brightness values were 79-80% for the acetylated sheets compared to 60-62.5% for the controls after an intense aging for 312 and 349 hours. The reduced absorption at λ_{max} just below 400 nm (extending into the visible range) indicates that some of the colored structures formed on acetylation of high-brightness aspen CTMP most likely are readily photobleachable when subjected to a light source emitting light in the visible range. Also, the acetylated spruce CTMP, irradiated with the RPR 4190Å and RPR 5750Å UV/VIS-fluorescent lamps, removed structures contributing to the absorption just below 400 nm. The apparent absorption maxima at 425 nm observed for irradiated unacetylated spruce CTMP was practically missing after acetylation, except for the low derivatized CTMP (see Figs. 7b-c).

These results indicate that acetylation slows down the UV-light induced reactions as seen for the RPR 3500Å UV-lamps aged CTMPs. However, acetylation promotes photobleaching reactions when subjected to an irradiation source emitting light in both the ultraviolet and visible regions, an effect that contributes to the improved stability toward light-induced aging. These results also indicate that different photochemical reactions occur, depending on the light source used for reversion, for acetylated pulps as well as for unacetylated pulps. It is therefore extremely important to use a light source that mimics the actual aging conditions as close as possible if an accurate picture of the yellowing phenomenon is going to be obtained. Further studies, using both unacetylated and acetylated model compounds incorporated on different types of high-yield pulps, are needed to fully explain the changes in the absorption difference spectra of acetylated and/or irradiated high-yield pulps.

Conclusions

This work demonstrates the usefulness of solid-state UV/VIS diffuse reflectance spectroscopy for the study of light-induced brightness reversion of untreated and chemically modified high-yield pulps. This work also shows the importance of the irradiation source used for accelerated aging because the photochemistry is strongly dependent of the wavelength distribution of the light source chosen.

Acetylation of aspen CTMP was found to generate a substantial increase in absorption in the entire wavelength region of 350-700 nm with maxima at approximately 370 and 430 nm, whereas the changes that took place during acetylation of the spruce CTMP were manifested as a decrease in absorption at wavelengths below 410 nm (maximum at 385 nm) and an increase in the absorption band centered at 455 nm.

UV-irradiation of aspen CTMP introduced chromophores with an absorption maxima near 370 nm and with a shoulder at approximately 415 nm. When the aspen CTMP was irradiated with the UV/VIS lamps, a slight shift in the absorption peak to shorter wavelengths (λ_{max}~360 nm) together with less absorption in the visible range was observed. The absorption difference spectra of UV-irradiated spruce CTMP displayed two absorption bands at 330 and 425 nm. In addition to these two bands, UV/VIS-irradiation induced photobleaching in the UV-part of the spectra extending into the visible range (λ_{max}~390 nm). Acetylation of the pulps slowed down the

UV-light induced chromophore formation, but could also promote photobleaching if the acetylated pulps were subjected to both UV-radiation and visible light.

It is difficult to access the changes seen in the UV/VIS spectra to the formation/destruction of chromophoric and leucochromophoric structures in the lignin since i) most absorption data are given for simple model compounds in solution, and it is likely that the position of the absorption peeks may be different in the solid phase, and ii) the position of absorption maxima of the chromophoric and leucochromophoric structures may be shifted when incorporated in the lignin macromolecule. Further studies are therefore needed to determine the absorption characteristics of several classes of important structures when incorporated in different types of high-yield pulps.

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Figure captions

Fig. 1. Spectral characteristics of the tested irradiation sources. The spectral energy distributions of standard "cool white" fluorescent color (Waymouth 1992, dotted line) and natural daylight (Merrigan 1975, broken line) are given as a comparison.

*Fig. 2. Absorption difference spectra of hydrogen-peroxide-bleached aspen CTMP after irradiation for various periods of time ($\Delta ABS = ABS_{irradiated} - ABS_{unirradiated}$). **a**: RPR 3500Å. **b**: RPR 4190Å. **c**: RPR 5750Å.*

*Fig. 3. Absorption difference spectra of hydrogen-peroxide-bleached spruce CTMP after irradiation for various periods of time ($\Delta ABS = ABS_{irradiated} - ABS_{unirradiated}$). **a**: RPR 3500Å. **b**: RPR 4190Å. **c**: RPR 5750Å.*

Fig. 4. Absorption difference spectra of hydrogen-peroxide-bleached spruce CTMP ($\Delta ABS = ABS_{irradiated} - ABS_{unirradiated}$). RPR 3500Å: 7 h. RPR 4190Å: 349 h. RPR 5750Å: 312 h.

Fig. 5. Absorption difference spectra of hydrogen-peroxide-bleached aspen CTMP (solid line) and hydrogen-peroxide-bleached spruce CTMP (dotted line) after acetylation ($\Delta ABS = ABS_{acetylated} - ABS_{unacetylated}$). The numbers in brackets denote the acetylation time in minutes.

*Fig. 6. Absorption difference spectra of hydrogen-peroxide-bleached aspen CTMP after acetylation (acetyl content: 8.1%) and subsequent irradiation for various periods of time ($\Delta ABS = ABS_{acetylated,\ irradiated} - ABS_{acetylated,\ unirradiated}$). The dotted line shows the absorption difference spectra for a low derivatized aspen CTMP (acetyl content: 3.9%). **a**: RPR 3500Å. **b**: RPR 4190Å. **c**: RPR 5750Å.*

*Fig. 7. Absorption difference spectra of hydrogen-peroxide-bleached spruce CTMP after acetylation (acetyl content: 9.6%) and subsequent irradiation for various periods of time ($\Delta ABS = ABS_{acetylated,\ irradiated} - ABS_{acetylated,\ unirradiated}$). The dotted line shows the absorption difference spectra for a low derivatized spruce CTMP (acetyl content: 4.4%). **a**: RPR 3500Å. **b**: RPR 4190Å. **c**: RPR 5750Å.*

Table 1. Change in optical properties [TAPPI brightness ($R_{\infty 457}$), L-, a*-, and b*-values] on acetylation and light-induced aging of untreated and acetylated hydrogen-peroxide-bleached aspen CTMP and spruce CTMP. Acetylation times (min) are given within parentheses.*

Pulp	Acetyl content, % by mass	Unirradiated				RPR 3500Å Irradiation time: 2 h/7 h[a]				RPR 4190Å Irradiation time: 349 h				RPR 5750Å Irradiation time: 312 h			
		$R_{\infty 457}$, %	L*	a*	b*	$R_{\infty 457}$, %	L*	a*	b*	$R_{\infty 457}$, %	L*	a*	b*	$R_{\infty 457}$, %	L*	a*	b*
Aspen CTMP																	
Control	0.6	84.3	96.4	-1.3	5.6	64.4	92.0	-1.8	14.4	62.6	90.6	0.0	13.6	60.0	89.8	-0.1	14.7
Acetylated (5)[b]	3.9	76.4	94.2	-1.0	8.0	63.4	91.7	-1.4	14.9	73.4	93.6	-0.4	9.4	72.7	93.6	-0.4	9.9
(20)[b]	8.1	73.1	93.6	-0.5	9.4	63.7	91.8	-0.8	14.8	80.2	95.1	-0.3	6.4	78.9	94.9	-0.4	7.1
Spruce CTMP																	
Control	0.5	77.8	95.5	-1.9	9.3	48.5	88.6	-1.8	24.4	48.5	87.1	-0.6	21.6	46.7	86.5	0.9	22.6
Acetylated (5)[b]	4.4	75.2	95.4	-1.8	11.1	51.8	90.4	-1.8	24.0	60.7	91.1	-0.7	16.4	60.4	90.8	-0.3	16.1
(20)[b]	9.6	73.3	95.0	-1.6	11.8	56.0	91.4	-2.0	21.4	73.1	93.8	-0.6	10.0	71.6	93.7	-0.7	11.0

[a] The data are given at an irradiation time of 2 hours and 7 hours for the aspen CTMP and spruce CTMP, respectively.

[b] Acetylation temperature, 100 °C.

Figure 1

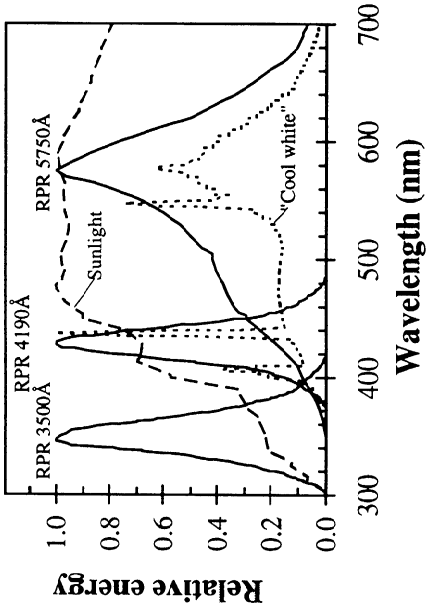

RPR 3500Å
RPR 4190Å
RPR 5750Å
Sunlight
Cool white
Relative energy
1.0
0.8
0.6
0.4
0.2
0.0
300
400
500
600
700
Wavelength (nm)

Figure 2a

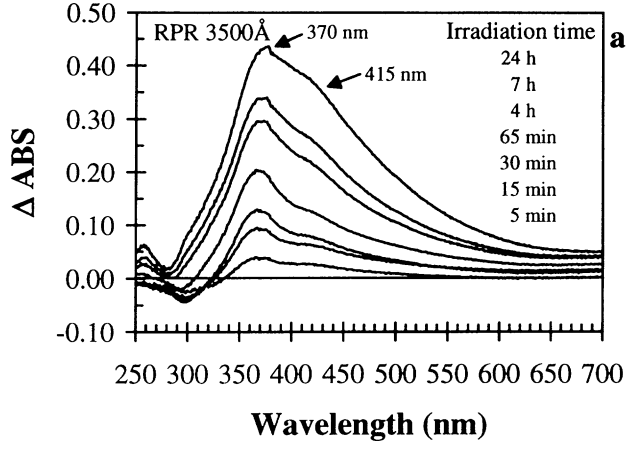

RPR 3500Å
370 nm
415 nm
Irradiation time
24 h
7 h
4 h
65 min
30 min
15 min
5 min
a
Δ ABS
0.50
0.40
0.30
0.20
0.10
0.00
-0.10
250 300 350 400 450 500 550 600 650 700
Wavelength (nm)

Figure 2b

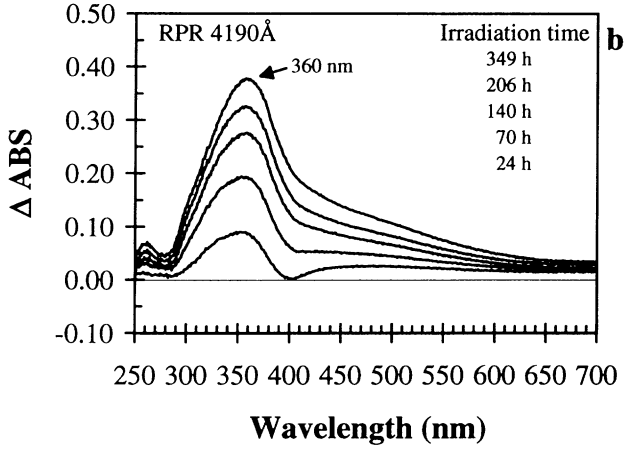

RPR 4190Å
360 nm
Irradiation time
349 h
206 h
140 h
70 h
24 h
b
Δ ABS
0.50
0.40
0.30
0.20
0.10
0.00
-0.10
250 300 350 400 450 500 550 600 650 700
Wavelength (nm)

Figure 2c

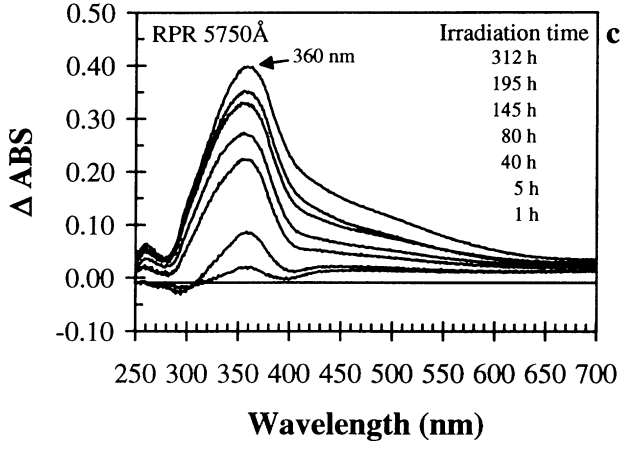

RPR 5750Å
360 nm
Irradiation time
312 h
195 h
145 h
80 h
40 h
5 h
1 h
c
0.50
0.40
0.30
0.20
0.10
0.00
-0.10
Δ ABS
250 300 350 400 450 500 550 600 650 700
Wavelength (nm)

Figure 3a

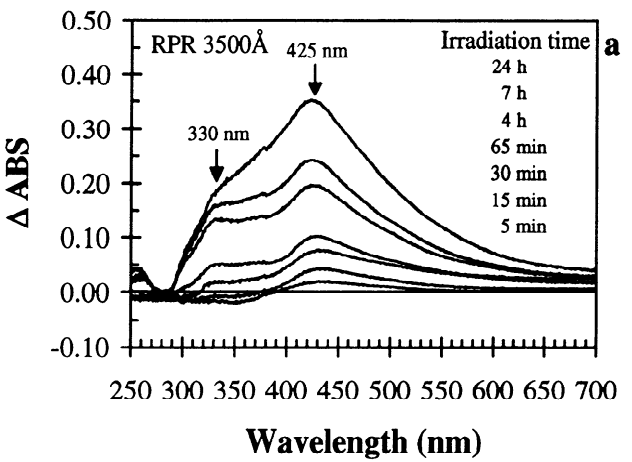

RPR 3500Å
425 nm
330 nm
Irradiation time
24 h
7 h
4 h
65 min
30 min
15 min
5 min
a
Δ ABS
0.50
0.40
0.30
0.20
0.10
0.00
-0.10
250 300 350 400 450 500 550 600 650 700
Wavelength (nm)

Figure 3b

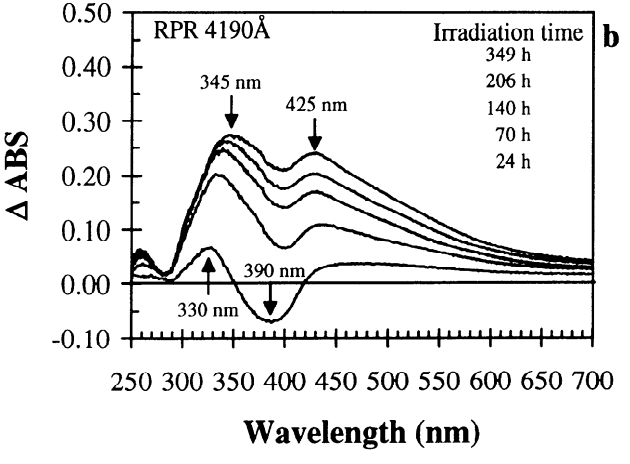

RPR 4190Å
Irradiation time
349 h
206 h
140 h
70 h
24 h
b
345 nm
425 nm
390 nm
330 nm
Δ ABS
0.50
0.40
0.30
0.20
0.10
0.00
-0.10
250 300 350 400 450 500 550 600 650 700
Wavelength (nm)

Figure 3c

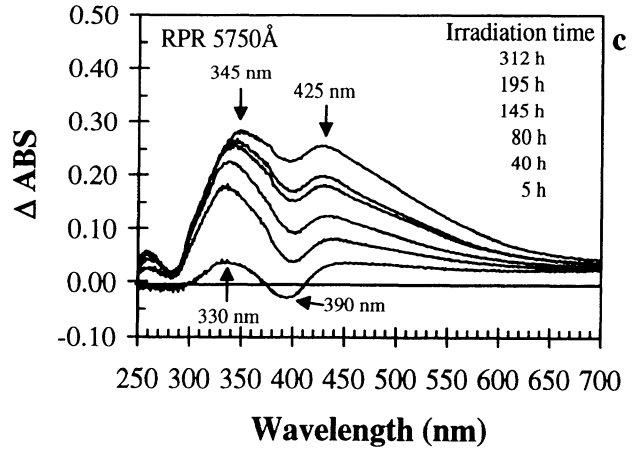

RPR 5750Å
Irradiation time
312 h
195 h
145 h
80 h
40 h
5 h
345 nm
425 nm
330 nm
390 nm
c
Δ ABS
0.50
0.40
0.30
0.20
0.10
0.00
-0.10
250 300 350 400 450 500 550 600 650 700
Wavelength (nm)

Figure 4

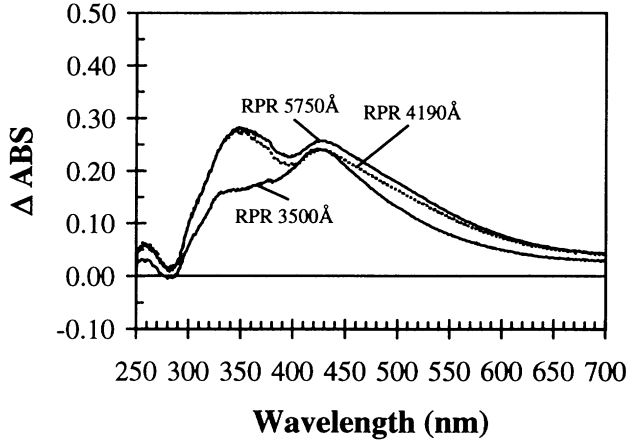

0.50
0.40
0.30
0.20
0.10
0.00
-0.10
Δ ABS
RPR 5750Å
RPR 4190Å
RPR 3500Å
250 300 350 400 450 500 550 600 650 700
Wavelength (nm)

Figure 5

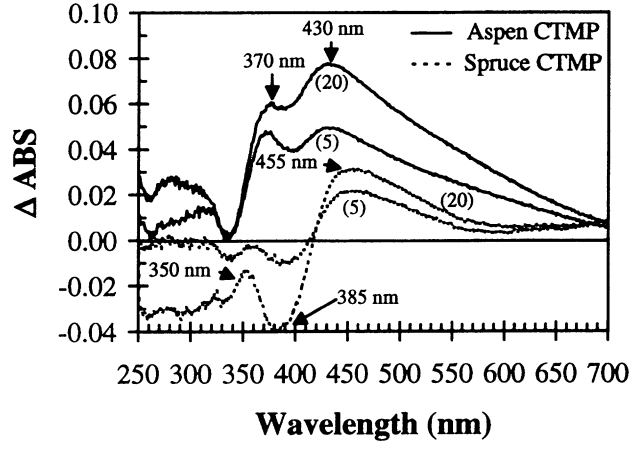

0.10
0.08
0.06
0.04
0.02
0.00
-0.02
-0.04
Δ ABS
430 nm
370 nm
(20)
(5)
455 nm
(20)
(5)
350 nm
385 nm
Aspen CTMP
Spruce CTMP
250 300 350 400 450 500 550 600 650 700
Wavelength (nm)

Figure 6a

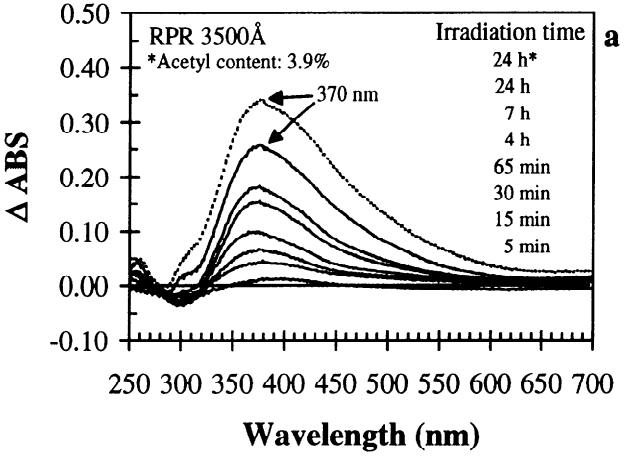

RPR 3500Å
*Acetyl content: 3.9%
370 nm
Irradiation time
24 h*
24 h
7 h
4 h
65 min
30 min
15 min
5 min
a
Δ ABS
0.50
0.40
0.30
0.20
0.10
0.00
-0.10
250 300 350 400 450 500 550 600 650 700
Wavelength (nm)

Figure 6b

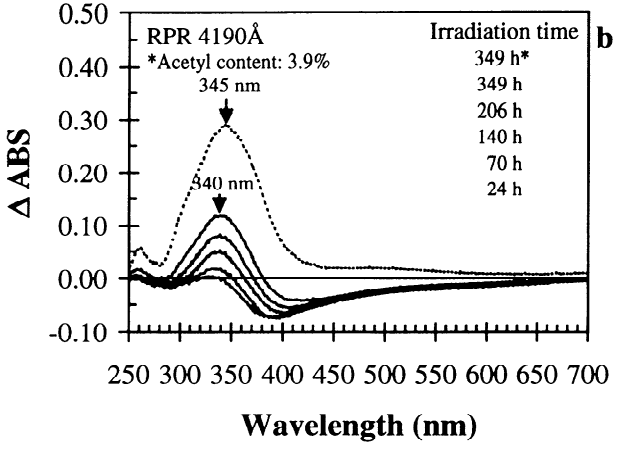

RPR 4190Å
*Acetyl content: 3.9%
345 nm
340 nm
Irradiation time
349 h*
349 h
206 h
140 h
70 h
24 h
b
Δ ABS
0.50
0.40
0.30
0.20
0.10
0.00
-0.10
250 300 350 400 450 500 550 600 650 700
Wavelength (nm)

Figure 6c

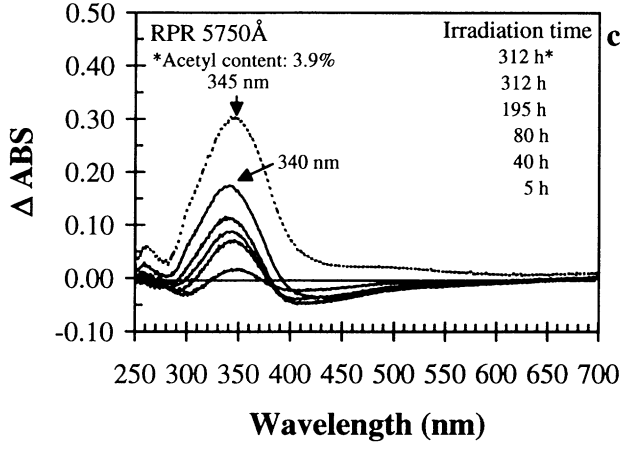

RPR 5750Å
*Acetyl content: 3.9%
345 nm
340 nm
Irradiation time
312 h*
312 h
195 h
80 h
40 h
5 h
c
Δ ABS
0.50
0.40
0.30
0.20
0.10
0.00
-0.10
250 300 350 400 450 500 550 600 650 700
Wavelength (nm)

Figure 7a

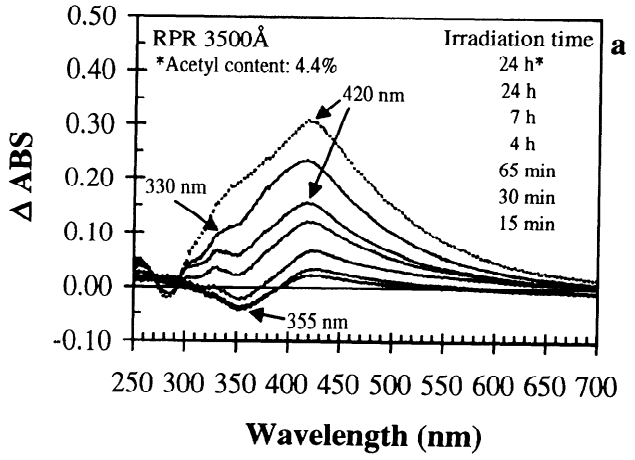

RPR 3500Å
*Acetyl content: 4.4%
Irradiation time
24 h*
24 h
7 h
4 h
65 min
30 min
15 min
a
420 nm
330 nm
355 nm
Δ ABS
0.50
0.40
0.30
0.20
0.10
0.00
-0.10
250 300 350 400 450 500 550 600 650 700
Wavelength (nm)

Figure 7b

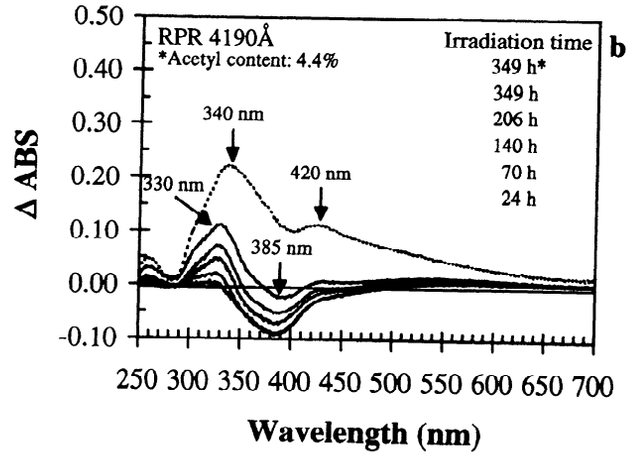
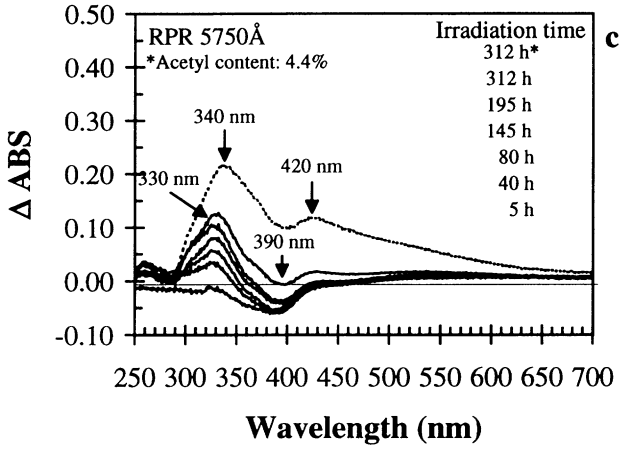

RPR 4190Å
*Acetyl content: 4.4%
Irradiation time
349 h*
349 h
206 h
140 h
70 h
24 h
b
340 nm
330 nm
420 nm
385 nm
Δ ABS
0.50
0.40
0.30
0.20
0.10
0.00
-0.10
250 300 350 400 450 500 550 600 650 700
Wavelength (nm)

Figure 7c


RPR 5750Å
*Acetyl content: 4.4%
Irradiation time
312 h*
312 h
195 h
145 h
80 h
40 h
5 h
340 nm
330 nm
420 nm
390 nm
c
ΔABS
0.50
0.40
0.30
0.20
0.10
0.00
-0.10
250 300 350 400 450 500 550 600 650 700
Wavelength (nm)

IMPROVED STEM GROWTH RATES AND FIBER PROPERTIES:

FUNDAMENTAL BIOLOGICAL MECHANISMS

Gary Peter
Douglas Benton

March 25-26, 1998

Improved Stem Growth Rates and Fiber Properties: Fundamental Biological Mechanisms

Gary Peter, Assistant Professor
Douglas Benton, MS expected '99

SUMMARY:
A new direction is being taken in the forest biology research program. In addition to our work on the somatic embryogenesis of loblolly pine, we are also focusing on the mechanisms that control wood fiber properties, with the future intent at improving stem growth rates, fiber processing and fiber properties for adding value to products. One current target for our work is to understand the biological mechanisms that control the cellulose microfibril angle (MFA). Cellulose MFA is a major determinant of fiber strength, as well as paper and wood dimensional stability. We potentially have developed a rapid and simple light microscopic method for measuring the microfibril angle in southern pine trees that can be used for analysis of this important aspect of wood quality.

RESEARCH LINE/ROADMAP: (New from Spring 1998)

Area	Improved Forest Productivity
Research Line	Develop fibers with properties similar to or better than Northern softwood and Eucalyptus which can be grown in most regions of North America.
Road Map	Develop fundamental understanding of secondary wall differentiation and stem growth

OBJECTIVES:

This project has three broad objectives:

1) Increase stem growth rates
2) Improve fiber properties for value added paper products
3) Improve the processing characteristics of wood to decrease environmental impacts while increasing fiber yield and pulp quality

Since our understanding of the biological mechanisms that regulate cambial cell growth rate, xylem fiber and secondary cell wall properties is so limited, to accomplish these goals a more fundamental understanding of the biochemical, cellular and molecular genetics in each of these areas must be obtained first.

BACKGROUND:

Importance of Microfibril Angle. One of the most important properties of southern pine or softwood in general is high fiber strength. Strong agreement exists between experimental and theoretical studies relating MFA to strength and stiffness of paper. The MFA of fibers strongly influences the mechanical properties of paper. MFA and strength are related by a 4^{th} power dependency (1). Thus, a change of 10° in MFA produces a ~1000 kg/mm^2 change in longitudinal Young's modulus (2). Low MFA pulps produce stronger, high modulus and less elastic papers than

do high MFA pulps. The strength properties make paper less susceptible to distortion and tensile failure during paper making and improve the quality the final products.

Measuring Microfibril Angle. A number of methods have been used to measure microfibril angle, including polarizing microscopy of mercury filled fibers (3) and of sectioned fibers (4); X-ray diffraction (5); radial pit aperture (6); UV shadowing (7); and most recently confocal laser scanning microscopy (8). Each of these methods has both advantages and disadvantages. For example, filling fibers with mercury is not a particularly safe method, while X-ray diffraction is not a simple method, and the confocal method although rapid requires expensive equipment. In general what is needed for plant breeding purposes is a very rapid and accurate method that requires only limited preparation of the fiber.

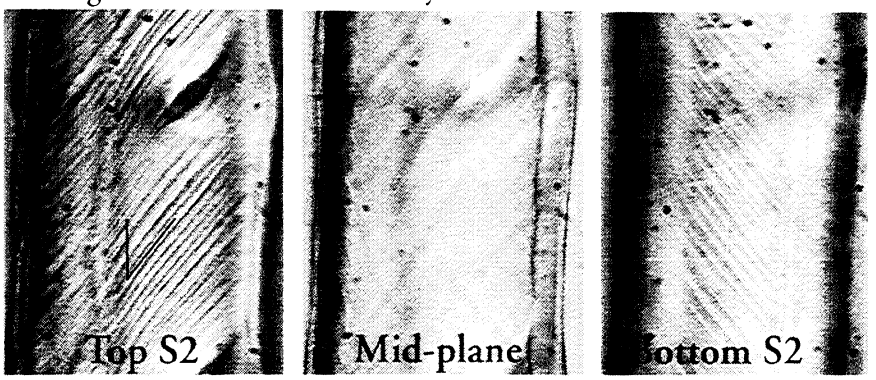
Variation in Microfibril Angle. A number of general trends have been observed for the MFA in the S2 layer of softwood tree fiber cells. For example, MFA is higher in fibers obtained from juvenile than mature wood (9). It also is higher in earlywood fibers when compared to latewood fibers and from fibers obtained from higher up on the tree when compared to ones within the same growth ring lower down on the tree (9). MFA is influenced both by genotype (10) and the growth environment even in existing trees (11). For rapid growth on plantations will have high MFA overall because the wood is predominately juvenile and more like spring wood. This high MFA lowers the quality and usefulness of this wood.

Regulation of Microfibril Angle. The overall regulation of MFA is complex due to its variation within a single tree, but a general cellular mechanism that controls MFA is well documented. Deposition of cellulose microfibrils is determined by the position of microtubules that lie just inside of the plasma membrane, the cortical microtubules (12). Changes in the organization of cortical microtubules produce changes in the pattern of cellulose deposition. However, the genetic and molecular mechanisms that regulate cytoskeletal organization within differentiating xylem tracheids are completely unknown.

RESULTS:

To breed for trees with lower MFA in juvenile wood that is fast growing, we need a method to accurately and rapidly measure MFA. At IPST we believe that we have developed a simple and rapid method for determining MFA. Figure 1 below shows three planes of the same juvenile fiber from loblolly pine. Small wood pieces were delignified with acetic acid/hydrogen peroxide, the fibers were gently separated, mounted in water and visualized directly by high resolution light microscopy.

Figure 1. S2 MFA of Loblolly Pine Mature Wood Tracheid



Validation of Method: We are currently comparing, in the same single fibers, the results obtained with this simple and rapid method with those obtained from other more accepted methods; polarizing microscopy and confocal laser scanning microscopy. We are confident that when the S2 layer is thick that we can we accurately measure the MFA of the S2 layer. With this method we have not been able to measure the MFA in the S1 or S3 layers since they are not of sufficient thickness.

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SOUTHERN PINE MECHANICAL PULP

Status report for Project F012

Alan Rudie
Lars Johansson

March 25-26, 1998

DUES-FUNDED PROJECT SUMMARY
FY 1997-98

Project Title: Southern Pine Mechancial Pulp
Project Code: SPMP
Project Number: F012
PAC: High Yield Pulping
Division: Chemical and Biological Sciences Division
Project Staff
Faculty/Senior Staff: Alan Rudie, Lars Johansson
Staff:
FY 97-98 Budget: $100,000
Allocated as Matching Funds: No
Time Allocation
Faculty/Senior Staff: AWR 20%
LJ 100%
Support: 55%
Supporting Research
M.S. Students: Jeff Byrum (Southern Hardwood APP)
Aaron Yonka (Use of CTMP in paperboard grades)
Ph.D. Students: Cherryl Rueckert (Energy absorption in fiber aggregates)

External: Gunnar and Lillian Nicholson Fellowship

RESEARCH LINE/ROADMAP: 3: Increase the yield of kraft-pulp equivalent fiber by ten percentage points.

- Develop techniques to modify fiber sources for high yield pulps
- Develop modified/new pulping/bleaching processes - High yield mechanical strength.

PROJECT OBJECTIVE: Improve the performance of the mechanical pulping process

PROJECT BACKGROUND: It is well known that high yield pulps are very sensitive to wood species and wood quality parameters such as tree age, specific gravity and growth rate. With the success of intensive forestry methods, and the advent of genetic engineering in trees, there is considerable value in understanding which features of wood and fiber morphology contribute to the properties of high yield pulps. Southern pine has been selected as a target species because the high latewood content and large growth increments allow visual observation in simulations of refining, and as a poor quality species, may better illuminate those features of fiber morphology that are detrimental to high yield pulp quality.

SUMMARY OF RESULTS:

Samples of TMP prepared from forest grown and plantation grown loblolly pine have been evaluated for traditional handsheet properties as well as hydrodynamic specific surface, lignin content, surface lignin coverage, specific bond strength and optical bonded and non-bonded area. The two samples do not exhibit typical plantation wood TMP behaviors in that the pulp produced from plantation grown wood was stronger than the pulp produced from the forest

grown wood. The biggest difference in the pulps produced from the two wood samples is the relationship of freeness to hydrodynamic specific surface area. Normally, freeness is considered a measure of surface area, but in this capacity it is quite limited. With these samples, the TMP produced from the plantation grown trees has 45% more surface area at a given freeness than the TMP produced from forest grown trees. This also affects surface lignin and optical scattering coefficient. On the other hand, the pulp produced from the forest grown wood appears to have higher specific bond strength. The uncharacteristic behavior of the two samples limits the strength of any conclusions that can be drawn from the experiments, but the results do serve to identify those features of the wood and pulp that vary with the changes in TMP strength and are worthy of further study on a large enough group of samples to have statistical validity.

GOALS FOR FY 97-98:

Evaluate samples of wood chips for:

- specific gravity
- fibril angle
- fiber length

and primary and secondary refiners pulps for:

- bond strength/RBA
- surface area
- lignin content
- surface lignin coverage

Attempt to correlate the variation in pulp quality to these parameters.

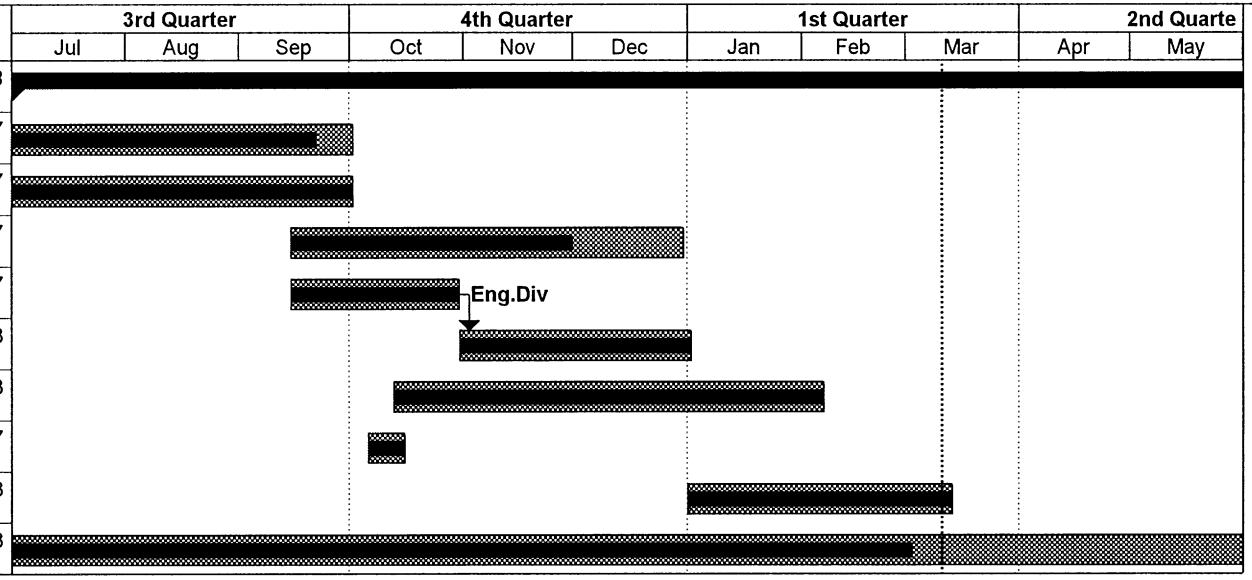
DELIVERABLES: A list of key chemical or physical parameters that dominate the quality issue of converting softwoods to thermomechanical pulp.

SCHEDULE (Attach Timeline):

	Target	Completion
1. Receive/collect samples:	(5/1 to 9/30/98)	2/3 (no spruce)
2. Complete standard handsheet testing:	(10/30/98)	yes
3. Complete surface testing:	(1/30/99)	yes
4. Complete Klaison's lignin analysis	(1/30/99)	yes
5. Complete surface lignin analysis	(2/30/99)	yes

Project F012, Southern Pine Mechanical Pulping

ID	Task Name	Finish
1	**Poor Strength, Juvenile TMP**	**Tue 6/30/98**
2	Obtain pulps	Wed 10/1/97
3	initial testing/setup	Wed 10/1/97
4	Measure RBA/Spec. Bond Str	Tue 12/30/97
5	Specific surface equip. repair	Thu 10/30/97
6	Pulp surface area	Thu 1/1/98
7	measure surface lignin	Fri 2/6/98
8	Measure Total Acid Group	Wed 10/15/97
9	Measure Fibril Angle	Fri 3/13/98
10	project reporting	Tue 6/30/98



Project:
Date: Wed 3/11/98

Task
Progress
Milestone
Summary
Rolled Up Task
Rolled Up Milestone
Rolled Up Progress

ANNUAL REVIEW: PROJECT F012
Southern Pine Mechanical Pulping

By: Lars Johansson and Alan Rudie

ABSTRACT

The TMP properties of mature and juvenile wood from loblolly pine are examined. Samples of fresh loblolly pine chips and TMP pulps from primary, secondary and tertiary refining stages were obtained. The wood was from both juvenile stands (15 years old) and mature stands (33 years old). The wood was characterized and both the fiber length and the microfibril angle of the S_2 layer were measured. It was found that the sample of wood from the juvenile stand had somewhat higher average fiber length compared to the mature wood.

The thermomechanical refining of the chips was conducted on pilot scale refiners with the primary stage carried out using a 12" pressurized refiner and the following stages using a 36" atmospheric discharge refiner. Handsheets were made from the pulps and they were tested. Suprisingly the juvenile pulps were found to have both higher tensile strength and light scattering coefficient. To further investigate the reason for this, the specific surface area of the fibers was measured and the pulps from the juvenile stands had much higher specific surface area when compared at the same freeness level.

The surface lignin of the pulp fibers was measured by sulfonation of the lignin followed by polyelectrolyte titration with a large cationic polymer. The mature pulps had a higher content of surface lignin than the pulps produced from the juvenile wood. It is proposed that this can be one explanation for the low bond strength of the TMP's produced from the mature wood sample.

INTRODUCTION

As a tree grows from a sapling to a mature tree, many physical and anatomical features of both the wood and wood fibers change. The juvenile wood in a tree is defined as wood produced by a young cambium. The rather different physical properties of juvenile wood usually cause manufacturing challenges in production of mechanical pulp. Because plantation grown trees grow rapidly and reach merchantable size at an early age, a very high proportion of the tree is composed of juvenile wood. Since plantation wood is comprising an increasing larger share of the raw material source, an awareness of the juvenile wood properties which control end-product performance is essential.

When analyzing the freeness scattering relationship, the evidence from the existing project[1] suggests that TMP from low density (juvenile, or plantation grown) southern pines have lower relative bond strength than TMP from average density southern pines. One explanation for this can be that a relative high level of surface lignin could interfere with the bond strength. In order to evaluate if there is a difference in surface lignin content

between pulps from juvenile and mature wood and how this affects the strength properties, samples from both types were collected and both the raw material as well as the thermomechanical pulps were analyzed and characterized.

PRIOR YEARS RESULTS:

The long term objective of this project is to understand the chemical and morphological features of wood that contribute to pulp strength in high yield pulps. The project concentrates on southern pine since it generally produces a weak TMP and has considerable within species variation to work with. Spruce is used as a reference when available and useful for the project task, and juvenile pine or plantation grown pine is used to help understand the within species changes that affect strength.

A chlorite holopulping technique was developed during the fiscal year 1991 to establish a method for evaluating fiber strength throughout the high yield pulping process. This technique was subsequently used successfully to evaluate strength losses in impregnators at one member companies mills, and track seasonal TMP strength changes at another member company mill. In evaluating seasonal strength properties, it became apparent that at least some of the strength changes were due to changes in the fiber supply of the mill, changes in the content of faster growth rate wood typical of plantation grown trees. Since this was becoming a pressing problem for several member companies, the project reaffirmed, as part of the goal, to understand the differences in mature and juvenile/plantation loblolly pine that influence the development of paper strength in TMP.

In FY 94/95, the project evaluated the rate of breakdown of wood chips into fiber in refining. Using the pilot refining facilities at Andritz Sprout-Bauer, samples of plantation grown (6 years old), and forest grown (14 years old) pine were refined using three sets of primary refiner plates. In two of the three sets of plates, portions of the perimeter bars were ground off to produce a pulp characteristic of the quality of the fiber part way through primary refining. This data was then evaluated using a comminution theory, to obtain rates of formation and destruction of the Bauer McNet fractions. The analysis showed that the juvenile wood developed long fiber (R_{28}) faster, but it also broke down faster (Figure 1). After about 1,500 kWh/ODT, the pulps produced form the plantation grown pine had less R_{28} and shorter average fiber lengths than the pulps produced from the forest grown wood. A control sample from spruce showed about the same rate of formation for R_{28} as the forest grown pine, but a much lower rate of R_{28} breakdown, and in the end, had the longest average fiber length.

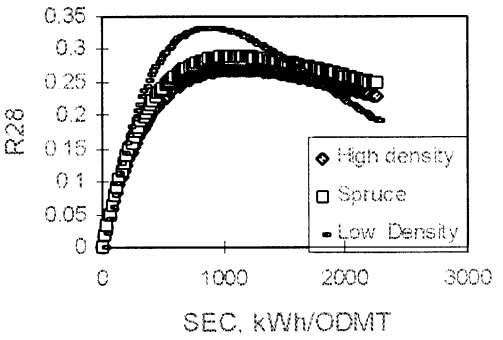


Figure 1. Formation and destruction of the R_{28} mesh fraction.

Although these differences were considered significant, they were not deemed big enough to cause the major differences in the strength of TMP produced from these three wood samples. A more thorough analysis of the strength and optical data suggested that at a given bond strength, there was a larger unbonded area in the pulps produced from the plantation grown wood. This suggests that relative bonded area is lower in these pulps. Two things about juvenile pine were suspect causes for the low RBA. A high fibril angle should cause a fiber to be more stiff in the radial direction, less able to collapse in the sheet of paper, and unable to bend readily to conform with the other fibers in the sheet. Seth *et al.* report fibril angles of 15.8 to 16.9 for Spruce and 23.9 for loblolly pine.[2] Generally, fibril angle decreases in trees as they mature. In a study of 50 loblolly pines from Louisiana, McMillin reports the fibril angle declined from an average 28° in the first ten growth rings, to 25.6° in growth rings 10 through 20.[3] Based on a recent report of differences in lignin distribution in several radiata pine clones and the influence this has on fracture surfaces[4] and TMP properties, it was decided to measure surface lignin content of the fibers as well.

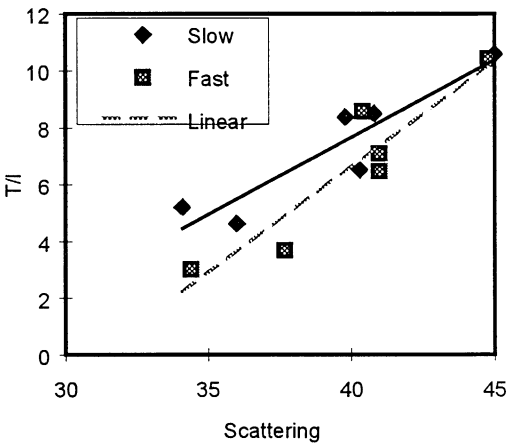


Figure 2. Sinkey bond index relative to scattering coefficient (unbonded surface area) for low and high density loblolly pine.

These observations and speculations led to the establishment of several tasks for the 97/98 fiscal year:

1. Evaluate lignin surface coverage of TMP fibers produced from plantation and forest grown samples of loblolly pine.
2. Evaluate/confirm the relationship between freeness and hydrodynamic specific surface for TMP produced from plantation grown and forest grown pine.
3. Evaluate RBA and specific bond strength in TMP form plantation and forest grown loblolly pine.
4. Determine fibril angle on the wood involved in the study.

EXPERIMENTAL

Material

Two wood samples were used in this investigation: Mature (33 years old) and juvenile (15 years old) samples of loblolly pine. Samples from primary, secondary and tertiary refining stages were collected for both the mature and the juvenile pulps and handsheets were prepared to evaluate the fundamental pulp properties.

Fiber length distribution

The fiber length distribution of the secondary and tertiary pulps was determined using the Kajaani FS-100®. The primary pulps, with a freeness of 660-690 ml CSF, had too many shives for direct Kajaani fiber length measurement and had to be delignified using the acid

chlorite process.[5] This process was also used for determining the average fiber length in the earlywood and latewood parts of both the juvenile and the mature chip samples.

Determination of the fibril angle

The fibril angle was measured on both earlywood and latewood samples from both the juvenile chips and the mature chips. The different wood samples were macerated at 60°C for three days in a mixture of hydrogen peroxide, water and glacial acetic acid (1:4:5 by volume) according to a method by Ruzin.[6] The separated fibers were mounted on slides and the microfibril angle of the S_2 layer was measured using a method developed by Peter.[7]

Total ion content

The total ion content of two samples from the mature and the juvenile pulps was measured according to the method of Katz et al.[8] The pulp was converted to the hydrogen form by soaking in 0.1 M HCl twice for 45 min and then washed with deionized water until a constant low conductance was reached. The pulp was then drained and dispersed in 0.001 M NaCl. The titration was done with 0.1 M NaOH dispensed from a burette while the pulp suspension was stirred under a nitrogen atmosphere.

To get better precision in the measurement of the strong acid content in the pulp, a known amount of 0.1 M HCl was added before the titration.

Surface Lignin concentration

The method for determining the surface lignin concentration of the fibers is based on sulfonation of the fibers, followed by polyelectrolyte titration of the sulfonic acid groups introduced into the lignin. The sulfonation of the fibers was carried out in pressure resistant glass vials containing 1 M Na_2SO_3-solution at 120°C, pH 9.7. The sulfonation time was 40 min which has been shown to be adequate to reach a plateau level in sulfonation.[9,10] The liquor to pulp ratio was 20:1. After sulfonation, the pulps where thoroughly washed with deionized water prior to surface charge measurement. The increase in surface charge after sulfonation is attributed to the introduction of sulfonate groups, whose content is assumed to be proportionally related to the lignin concentration of the pulp.

The surface charge measurement was based on an indirect polyelectrolyte adsorption method reported by Winter et al.[11] and by Wågberg et al.[12,13,14] The method is based on adsorption of a large positively charged molecule to the fiber surface. The cationic polymer used in this investigation was poly-dimethyldiallylammonium chloride (p-DMDAAC, CPS Chemical Company Inc.). In order to get a more narrow molecular mass dispersion of the cationic polyelectrolyte (p-DMDAAC), it had to be filtered before use and converted into its Br-form. To replace the chloride ions with bromide counter ions, a solution of the cationic polymer was treated in an ultrafiltration cell (Amicon membrane model 202) with a NaBr solution. The utrafiltration cell used was fitted with an Amicon YM 100 membrane with a molecular mass cut-off of 100 000 g/mol. The charge density of p-DMDAABr is $8.86 \cdot 10^{-3}$ eq/g.

The pore size distribution in cellulosic fibers has been studied by Stone and Scallan[15] and it has been shown that the average pore width is less than the size of this polymer.[16] Therefore it is reasonable to believe that p-DMDAABr only adsorbs at the surface of the pulp fibers. The concentration of acid groups determined by p-DMDAABr adsorption is thus considered to be a measure of surface acid groups in of the pulp fibers.

Prior to the adsorption experiments, the pulps were washed with 0.01M HCl to remove most of the metal ions and then with deionized water to pH 5. The sulfonic and carboxylic acid groups were converted to their Na^+-form by treatment with 0.001 M Na_2CO_3 and addition of NaOH to pH 9. To remove excess electrolyte, the pulps were washed with deionized water until the conductivity was less then 5 μS/cm. The fibers in their Na^+-form were suspended in deionized water to give a pulp suspension with a fiber concentration of 5g/l. The pH in the suspension was adjusted to pH 8 with 0.1 M NaOH.

Different amount of p-DMDAABr was added to a series of five pulp samples. The mixtures were stirred for 30 min under a nitrogen atmosphere in order to reach adsorption equilibrium. The pulp suspensions were then filtered on a Buchner funnel and the filtrates collected.

The concentration of p-DMDAABr in the filtrate was determined by titration with KPVS (potassium polyvinylsulfate) using OTB (orthotoluidine blue) as indicator. Knowing the total amount of charged polymers and the equilibrium concentration of the cationic polymer in the solution, the adsorbed amount can be calculated. By extrapolating the plateau level to zero equilibrium concentration, the adsorbed amount of polyelectrolyte at zero concentration can be obtained.

Determination of specific surface

The specific hydrodynamic surface was measured using the method reported by Lindsay.[17] Handsheets with a basis weight of 100g/m^2 were made and pressed once for 5 min at 345 kPa (standard first pressing for TAPPI[18] handsheets). The transverse permeability was then determined by compressing the water saturated pulp sample between two felts. Knowing the flow through the sample, the pressure drop over the sample and the thickness of the sample, the specific hydrodynamic surface area could be determined according to the Kozeny-Carman equation.[19,20]

Wet pressing

Sheets with a basis weight of 100 g/m^2 were made in a laboratory sheet former with white water recirculation. The sheets were pressed once at 97 kPa for 30 s and after changing the blotters, at pressures from 1100-4400 kPa for 60 s. They were dried at 60°C and then conditioned at standard conditions (50 % RH, 23°C) before testing. The sheets that were solvent exchanged were formed in the sheet former and then solvent exchanged in two stages with acetone and tert-buthyl methyl ether. The amount of solvent in each stage corresponded to about 40-50 times the volume of liquid in the sheets. The sheets were then allowed to dry.

RESULTS AND DISCUSSION

Wood properties

The loblolly pine samples were received as chips and pulps from the primary, secondary and tertiary refiner stages. The wood parameters of the chips are summarized below in Table 1. The juvenile zone in loblolly pine normally includes the first 7-10 growth rings.[21] One investigation[22] found that the amount of juvenile wood in a 15 year old stand of loblolly pine was 85 volume-% and in a 25 year old stand the amount of juvenile wood was 55 volume-%. In reality there is no sharp demarcation between the mature and the juvenile zone and within each zone the physical properties also change. This is especially true for the juvenile zone which is characterized by rapid changes in anatomical, chemical and physical properties.[23]

Table 1: Wood characterization.

Wood	Specific Gravity (g/cm^3)	Latewood (%)	Ring Width (mm)	Age (Years)
Mature Pine	0.46	48.2	3.1	33
Juvenile Pine	0.41	41.5	7.0	15

The fiber length of the wood was higher for the juvenile samples than for the mature samples (Table 2). This is not typical for juvenile and mature wood. Usually the tracheid length is shortest next to the pith. The tracheid length then increases outward with age.[24] This means that the mature part of a tree normally has higher average tracheid length than the juvenile part. The samples in this investigation do not follow this pattern, but it is known that a considerable between-tree variation exists. In both samples the latewood fibers were slightly longer than the earlywood fibers and this has been confirmed in other investigations.[25]

Table 2: Average fiber length and microfibril angle of the S_2 layer of earlywood and latewood from both juvenile and mature wood.

Wood sample	Fiber length, (mm)	Microfibril angle, (°)
Mature, Earlywood	2.95	35
Mature, Latewood	3.04	27
Juvenile, Earlywood	3.12	48
Juvenile, Latewood	3.19	34

The microfibril angle varies within the cell wall and within the tree. The higher microfibril angle in the S_2 layer of earlywood and juvenile wood fibers, observed for many conifers,[26,27,28] is closely connected to lower tensile strength of the fibers.[28] This is

important for chemical pulps where the role of fiber breakage during strength testing is considerable. The main mechanism of failure in papers made of mechanical pulps being bond failure,[29,30] the effect of microfibril angle is likely not to be as critical. The results found here (Table 2) are in agreement with earlier investigations of loblolly pine.[3]

Pulp properties

The general properties of the pulps are summarized in the Appendix, Table 1-2. When comparing the properties of the two types of pulp there are small differences. The difference in fiber length which was found for the wood still exists for the pulp samples.

The juvenile pulp samples have slightly higher average fiber length. This is also evident when comparing the results from the Bauer McNett fractionation. The juvenile sample has higher content of long fibers (+ 28). Both sets of pulp have consumed about the same amount of energy to a given freeness.

As seen in Figure 1, it is evident that the juvenile sample in this case has significantly higher tensile strength compared to the mature sample. In comparison to samples produced earlier in the Andtriz Sprout Bauer pilot plant using the same regional wood source, the pulp samples produced from the juvenile wood are quite similar in tensile at a given pulp freeness. At the same freeness, the samples produced from the mature wood source for this study are 30% lower in tensile strength compared to the samples produced at Andritz.

The difference in light scattering coefficient is much less profound, but the juvenile sample has slightly higher values when compared at the same freeness (Figure 2). This is similar to the results obtained at Andritz.

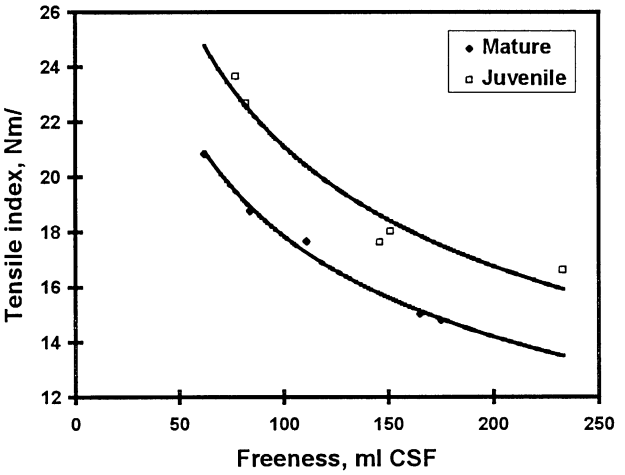


Figure 1: Tensile index versus freeness for mature and juvenile pulp.

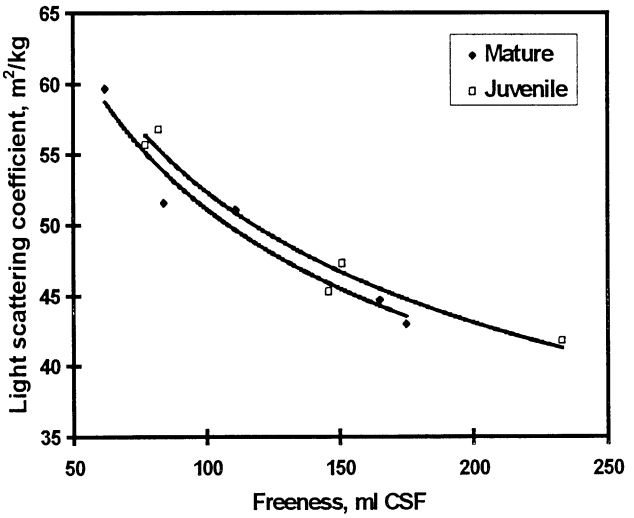


Figure 2: Light scattering coefficient versus freeness for mature and juvenile pulp.

These results were not expected for the two sets of pulps, but it was decided to continue the investigation and try to find the reason for the difference in strength properties.

The mature pulp sample nr. 2 (165 ml CSF) had by far the lowest specific surface area of the four investigated pulps (Table 3). As the refining continues from secondary to tertiary stage, the specific surface is increased. When comparing pulps with almost the same freeness it is evident that the juvenile samples have much higher specific surface area. This is probably due to the higher content of earlywood fibers in the juvenile wood. The higher fines content in the mature samples (cf. Table 1-2, Appendix) has not resulted in higher specific surface area for these pulps.

Table 3: Specific surface area.

Pulp sample	Freeness, ml	Specific surface area, (m^2/g)
Mature pulp (2)	165	5.5
Mature pulp (5)	84	11.6
Juvenile pulp (8)	146	11.3
Juvenile pulp (11)	82	16.9

Bonded area by wet pressing

The bond strength between fibers is dependent on the area of the bond as well as its specific strength. Both of these are determined largely by the conformability of the fibers, the geometry of the fiber surfaces, the externally applied pressure and the surface tension forces developed during drying.

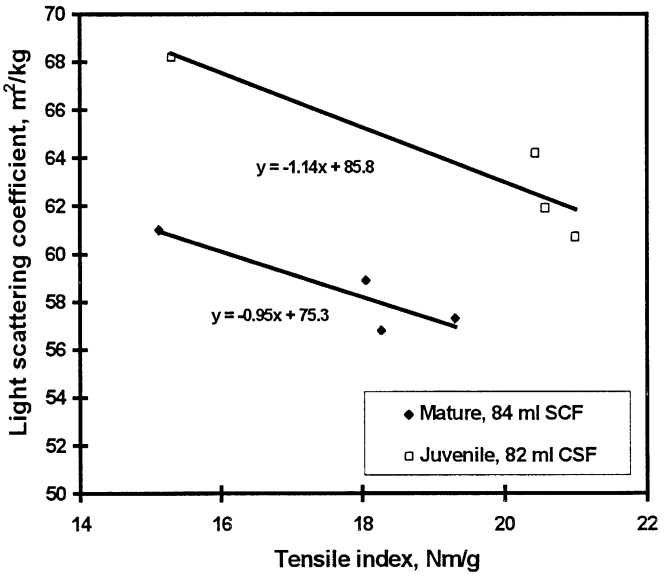


Figure 3: Light scattering coefficient versus tensile index after wet pressing and solvent exchange.

The total surface area of the dry fibers can be obtained by extrapolating the light-scattering coefficient to zero tensile strength. By changing the wet pressure after sheet formation different tensile strengths (i.e. different amount of bonded area) can be achived. Several methods have been suggested for obtaining very low bonded sheets. The method selected is to replace the water in the sheet with an organic solvent. The number of hydrogen bonds between the fibers is reduced, but some still form because of the atmospheric humidity.[31]

The results from applying different wet pressure on the sheets are shown in Figure 3. The light scattering coefficient increased with decreasing wet pressure, but to change the light scattering coefficient dramatically it is not enough just to vary the wet pressure. Even after solvent exchange the sheets have a significant tensile index. In order to get the total surface area of the pulps, the line for the light scattering coefficient can be extrapolated to zero tensile strength. The values shown in the equation for the lines in Figure 3 show the same result as found by measuring the specific hydrodynamic surface. That is that the total specific surface area is significantly higher for the juvenile pulp. The bond area calculated after extrapolation (Figure 4) reveal that the mature pulp have lower bond area when compared at the same tensile index. This suggests that the specific bond strength is in fact higher for the mature pulp fibers than for the juvenile pulp fibers.

Ion content

It has been shown that the strength properties of pulp are closely related to the ion content,[32] in particular the surface charge of the pulp.[16,33] While a high ion content contributes to swelling of fibers and thus an increased bonded area, ionized surface acid groups provide the fibers with increased bond strength per unit area.

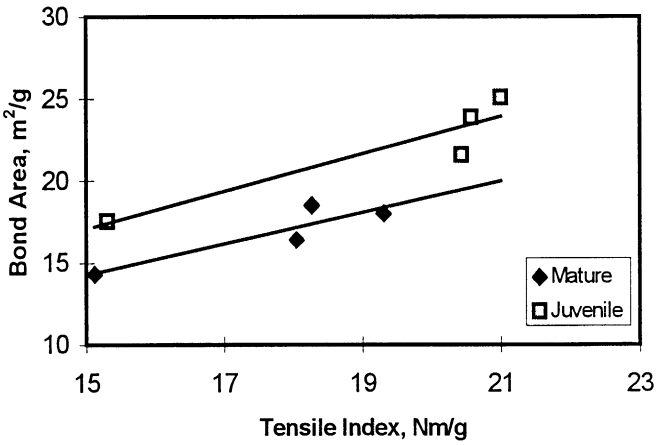


Figure 4: Bond area versus tensile index, calculated after extrapolation.

The total ion content for two of the mature and two of the juvenile samples are shown in Table 4. For these TMP pulps the total ion content is mainly carboxyl groups in the hemicellulose. There does not seem to be much difference in the total ion content between the two wood sources. In both cases the total ion content is slightly higher for the pulp with the higher freeness.

Table 4: Total ion content before sulfonation.

Pulp sample	Total ion content, (mmol/kg)
Mature pulp (2), 165 ml CSF	137
Mature pulp (5), 84 ml CSF	120
Juvenile pulp (8), 146 ml CSF	139
Juvenile pulp (11), 82 ml CSF	120

Upon sulfonation, both the total ion content and the sulfonate content is increased (Table 5). The sulfonate content was slightly lower for the pulps with lower freeness. The slight increase in the amount of carboxyl groups for some of the pulps might be due to a

formation of these groups during the heating to allow for the sufonation reaction to take place. This increase has also been found by Katz et al.[8] after sulfonation of wood.

Table 5: Total ion content and sulfonate content after 40 min sulfonation.

Pulp sample	Sulfonate content (mmol/kg)	Total ion content (mmol/kg)
Mature pulp (2), 165 ml CSF	182	319
Mature pulp (5), 84 ml CSF	168	304
Juvenile pulp (8), 146 ml CSF	176	314
Juvenile pulp (11), 82 ml CSF	154	294

Surface charge

The adsorption isotherms for the two mature and the two juvenile samples are shown in Figure 5. It can be seen that these isotherms are of the high affinity type with a plateau level. As shown in Figure 5 it is pulp number 2 (mature) which shows the lowest adsorption level. This pulp had high total ion content (Table 4). The explanation for this can be the very low specific surface area which this pulp had (Table 3).

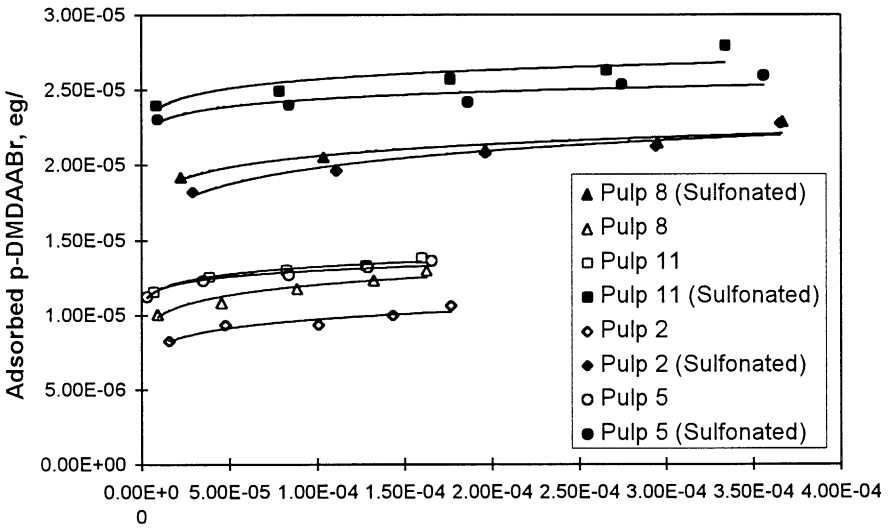


Figure 5: The adsorbed amount of p-DMDAABr (eq/g) as a function of equilibrium concentration of the polymer (eq/l) before and after sulfonation.

After sulfonation the adsorption levels are increased. The surface lignin concentration, described by the net increase in surface charge after sulfonation, can be calculated by using the Klason lignin content (Table 6). The results show that the juvenile pulp has slightly

lower percentage of surface lignin content. The surface lignin concentration can also be calculated based on the specific surface area of the fibers (Table 3) in each pulp. The results are shown in Table 6.

Table 6: Klason content and surface lignin concentration.

Pulp sample	Klason lignin content, (%)	Surface lignin content, (%)	Surface lignin conc., (g_{lignin}/m^2)
Mature pulp (2), 165 ml CSF	32.0	1.9	$3.5 \cdot 10^{-3}$
Mature pulp (5), 84 ml CSF	32.1	2.3	$2.0 \cdot 10^{-3}$
Juvenile pulp (8), 146 ml CSF	31.6	1.7	$1.5 \cdot 10^{-3}$
Juvenile pulp (11), 82 ml CSF	30.8	2.2	$1.3 \cdot 10^{-3}$

Taking into account the specific surface area of the pulp, the surface lignin concentration is reduced at lower freeness. This indicates that the new surfaces introduced by fibrillation have low lignin content. Fibrils that contribute to these surfaces derive mainly from the cellulose/hemicellulose-rich regions of the fiber wall.[34,35] When compared at constant surface area, the juvenile samples show significant lower surface lignin concentration than the mature samples. This was also in accordance with the mature samples lower strength properties (cf. Figure 1). Although the surface lignin concentration does not describe all the effects of low bond strength, it is one important factor to account for.

CONCLUSIONS

The results found in this investigation do not seem to be typical for juvenile and mature pulps but the method of analyzing the pulps has proved to be very useful. The unexpected results can be due to several reasons. One of the most obvious is that despite the normal higher density and lower microfibril angle for the mature wood, the juvenile wood had higher average fiber length. The higher Klason lignin content for the mature wood can also be one explanation. There are also a lot of strong equalizing mechanisms apparent in the development of strength between the fibers in the handsheet. The relative compliability and degree of collapse of the fibers are balanced by the consolidation and bond-reinforcing influences of the fines fractions.

The thin-walled fibers of loblolly pine juvenile wood might be expected to have some advantages over the thick-walled mature wood fibers. The thin-walled fibers can probably flex more easily during refining without reduction in fiber length.[36] The higher flexibility of the thin cell wall can also explain the higher sheet density and higher tensile strength for the juvenile pulp fibers found in the investigation. The increased fiber-fiber contact, from the greater specific surface area allows for tighter packing and a higher sheet density. The thick-walled and stiffer mature wood fibers have more difficulties to form such dense sheets. The high surface lignin content of the mature fibers will also interfere with the fiber bonding ability.

The complex nature of any analysis of relationships between wood and mechanical pulp properties is always evident. The heterogeneous nature of wood as raw material and the large variations between stems from different trees highlights the need for a large scale investigation to ensure significant results.

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APPENDIX

Table 1: Mature pulp properties.

Pulp sample, (number)		Primary (1)	Secondary (2)	Secondary (3)	Tertiary (4)	Tertiary (5)	Tertiary (6)
Specific energy, (kWh/t)		791	1611	1633	2501	2252	2030
Freeness, (ml CSF)		661	165	175	62	84	111
Fiber length, (mm)		2.11*	1.94	2.01	1.81	1.88	1.98
Pulmac shives, (% 4-cut)**		16.2	1.7	1.6	0.4	0.7	0.9
	14		9.2	9.7	5.6	7.8	7.7
	28		20.6	20.5	18.0	19.6	20.3
Bauer Mcnett	48		20.5	19.9	19.6	18.7	20.3
Classification, (%)**	100		13.6	13.5	14.1	14.1	14.2
	200		5.2	5.1	6.6	6.3	6.1
	-200		30.9	31.4	36.2	33.5	31.5
	L-factor		50.3	50.1	43.2	46.1	48.2
Density, (g/cm^3)			285	275	353	332	323
Tensile index, (Nm/g)			15.0	14.8	20.8	18.8	17.7
Tear index, (mNm^2/g)			5.8	5.1	6.3	5.6	5.7
Brightness, (%)			52.4	51.6	54.7	54.4	53.3
Opacity, (%)			86.2	84.3	93.1	89.0	88.4
Scattering coefficient, (m^2/kg)			44.7	43.0	59.7	51.6	51.1
Absorption coefficient, (m^2/kg)			2.3	2.3	2.7	2.4	2.5

Table 2: Juvenile pulp properties.

Pulp sample, (number)		Primary (7)	Secondary (8)	Secondary (9)	Tertiary (10)	Tertiary (11)	Tertiary (12)
Specific energy, (kWh/t)		831	1640	1456	2342	2313	1812
Freeness, (ml CSF)		693	146	233	77	82	151
Fiber length, (mm)		2.21*	1.95	2.05	1.90	2.02	2.02
Pulmac shives, (% 4-cut)**		20.9	1.6	3.1	0.8	0.8	1.4
	14		12.3	16.9	9.9	14.9	13.8
	28		22.3	23.4	19.6	19.8	21.8
Bauer Mcnett	48		18.0	18.1	17.1	16.3	18.2
Classification, (%)**	100		11.2	11.1	11.8	11.0	11.3
	200		4.3	4.4	6.0	5.7	5.0
	-200		32.0	26.1	35.6	32.4	29.9
	L-factor		52.5	58.4	46.6	50.9	53.9
Density, (g/cm^3)			297	274	352	347	361
Tensile index, (Nm/g)			17.6	16.6	23.7	22.7	18.0
Tear index, (mNm^2/g)			6.7	6.3	7.3	6.9	7.0
Brightness, (%)			56.7	55.0	58.7	58.8	57.1
Opacity, (%)			87.1	84.1	89.7	90.7	86.7
Scattering coefficient, (m^2/kg)			45.3	41.8	55.7	56.8	47.3
Absorption coefficient, (m^2/kg)			2.0	2.1	2.3	2.3	2.1

*Fiber length measured after chlorite holopulping.
** Measured at Champion International.